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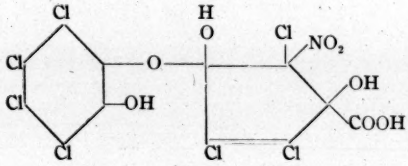
THE ACTION OF NITRIC ACID ON HEPTACHLOR-PYROCATECHINORTHOQUINO HEMIETHER[1]

BY C. LORING JACKSON AND G. L. KELLEY

The heptachlor hemiether, $C_6Cl_4(OH)OC_6Cl_3O_2$, when warmed with glacial acetic acid and a little fuming nitric acid, is converted into a new compound, $C_{12}H_4O_8NCl_7$, formed by the addition of the elements of a molecule of nitric acid and one of water to the original substance. It melts at temperatures between 176° and 198°, according to the speed with which it is heated, that is, according to the greater or less degree of decomposition it has undergone before the melting point is reached. Cases of this sort have been not uncommon in work on the orthoquinones, where most of the bodies decompose as they melt, but this substance and those related to it show this variation in an extreme form, so that the melting point is of no value in determining the purity of a compound. Accordingly, in order to get some criterion of purity, we purified seven specimens by different methods, and since analyses of these gave maximum differences of 0.78 per cent. on the chlorine and 0.88 per cent. on the carbon, we feel no doubt that our substance is a definite compound, and was pure.

[1] The work described in this paper formed part of a thesis presented to the Faculty of Arts and Sciences of Harvard University for the degree of Doctor of Philosophy by George Leslie Kelley.

In trying to determine the structure of this body we have encountered great difficulties—in fact, the publication of this paper has been delayed more than a year on this account, and even now the best graphic formula we have found is open to a serious objection; but, as it explains the other reactions of the compound satisfactorily, and there is much evidence that weakens the force of this objection, we feel justified in accepting this formula (I), according to which the substance is the tetrachlorpyrocatechin hemiether of 2-nitro-2,4,5-trichlor-1,3-dihydroxycyclopentene-1-carboxylic acid,



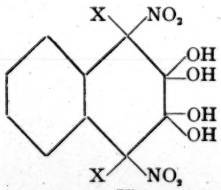
(I)

That this formula explains most of the reactions of the substance is shown by the following discussion of them: Tetrachlorpyrocatechin, $C_6Cl_4(OH)_2$, is easily obtained from it, or several of its derivatives, by the action of hydrochloric acid, sodic methylate, sodic hydroxide,[1] or even boiling water, and this easy breaking of the ether bond would be expected from its neighborhood to one of the hydroxyls.

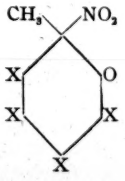
When acted on by acetic anhydride, acetyl chloride, sodic acetate in glacial acetic acid, sodic hydroxide, or even boiling water, an oxide of nitrogen and carbonic dioxide are split off. The removal of carbonic dioxide from cyclopentene-hydroxycarboxylic acids by the last two reagents has been observed by Zincke and by Hantzsch, but we have found no cases where it was removed by acetic anhydride or acetyl chloride, which, as a rule, have converted these substances into acetoxy acids. It seems possible, however, that a carboxyl surrounded by so many radicals as in our formula might be

[1] Chloranilic acid appeared sometimes during the action of sodic hydroxide and some other reagents on this compound, but this observation cannot be used in establishing its constitution, since it was proved by a special experiment that chloranilic acid can result from the action of these reagents on tetrachlorpyrocatechin.

decomposed with elimination of carbonic dioxide in the effort of the acetyl group to enter this part of the molecule. The ease with which our compound loses an oxide of nitrogen suggested at first that the nitric acid might be loosely attached, as in a compound of phenanthrenequinone, prepared by Kehrmann and Mattison,[1] or one of fluorenone made by Kurt H. Meyer,[2] but our substance shows no analogy to these, as they are red and decomposed by water quickly and completely, whereas ours is white, and attacked by water only when boiling and then slowly and partially. The easy removal of the oxide of nitrogen, especially by acetic anhydride or acetyl chloride, next seemed to us to point to the presence of a nitrite (—ONO), but the difficulty of obtaining the cycloketone, to be described later, from a nitrite was so great that we have come to the conclusion that our substance contains a nitro group, and its slight stability is not surprising when it is compared with the few analogous ring compounds we have found in the literature, which contain a nitro group attached to the same carbon with another radical. The only bodies we can find, in which this second radical is a halogen, are given by Zincke and Fries[3] (II),



(II)



(III)

and they are decomposed by heatihg with alcohol, glacial acetic acid, or strong sulphuric acid, and are therefore even less stable than our compound, which resists all these reagents. The quinitroles (III) are less closely related to our substance,

[1] Ber. d. chem. Ges., **35**, 343 (1902).

[2] *Ibid.*, **43**, 157 (1910).

[3] Ann. Chem. (Liebig), **334**, 342 (1904). Robertson and Briscoe [J. Chem. Soc., **101**, 1964 (1912)] have prepared a substance probably containing the group $C(NO_2)Cl$ which decomposed with alcohol or chloroform.

but undoubtedly belong to the same class. These lose their nitro groups by the action of benzene even in the cold, of moist cold ether, of acetic anhydride with 10 drops of sulphuric acid,[1] which is especially interesting in this connection, or of boiling glacial acetic acid,[2] so that they also are less stable than our compound.

Although the striking removal of carbonic dioxide and an oxide of nitrogen from our compound was brought about by many different reagents, we succeeded in isolating the organic product only, when acetic anhydride, or acetyl chloride, was used; and this was proved to be an acetyl compound,

$$C_{11}Cl_7O_3C_2H_3O$$

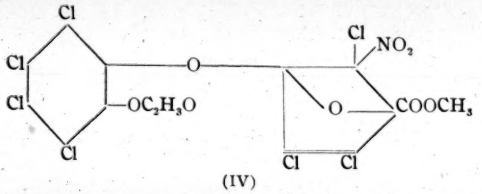
Subtracting from this the acetyl group and the tetrachlorpyrocatechin radical $C_6Cl_4O_2$, there is left C_5Cl_3O, which, according to its properties, can be only a five-carbon ring derived from that given in Formula I. A possible explanation of the mechanism of this reaction will be given later. Of the other reagents which produced this effect, the action of sodic hydroxide and of boiling water was to be expected, but, so far as we can find, the removal of carbonic dioxide and an oxide of nitrogen by sodic acetate dissolved in glacial acetic acid is without analogy, for in the few cases where sodic acetate has been used heretofore in related work it did not decompose the five-carbon ring acid. Possibly this difference in behavior may be due to the fact that our predecessors used it dissolved in water instead of in acetic acid.

When our substance was treated with methyl alcohol and sulphuric acid, a compound $C_{13}H_4O_7NCl_7$ was formed by the replacement of one hydrogen by methyl and the removal of a molecule of water; and this body gave a monoacetyl derivative with acetic anhydride, showing that the original substance contains 4 hydroxyls—one converted into methoxyl, two which lose water, and one converted into acetoxyl. This agrees with Formula I; and the acetyl compound is therefore the acetoxytetrachlorpyrocatechin hemiether of 2-nitro-

[1] Zincke, Breitwieser: Ber. d. chem. Ges., **44**, 176 (1911). Zincke: Ann. Chem. (Liebig), **394**, 1 (1912).

[2] Auwers: *Ibid.*, **302**, 163 (1898).

2,4,5-trichlorcyclopentene-1,3-oxide-1-carboxylic methyl ester (IV),



(IV)

It was observed that when a solution of sodic hydroxide was mixed with this ester, the oxide of nitrogen was removed only occasionally, the alkali not acting, as a rule, whereas the removal of the oxide of nitrogen from the free acid took place invariably. This observation is in harmony with our formulas, since nitric acid should be split off from (I) with great ease, but the nitrogen would be detached from (IV) only by a deep-seated reaction. The removal of water by the sulphuric acid and methyl alcohol in forming the ester is surprising in view of the fact that the free acid, after being heated to 100° with strong sulphuric acid alone for a whole day, was recovered unaltered on the addition of water. It should be observed that the want of agreement here is in the experimental results, and while we have found two possible explanations for it based on our formulas, they seem to us not sufficiently probable to be worth recording.

The chlorine in the original substance is firmly attached to the molecule, no hydrochloric acid being removed by sodic hydroxide or any of the other reagents already mentioned. When it is heated to fusion, however, our compound loses, in addition to carbonic dioxide and an oxide of nitrogen, one molecule of hydrochloric acid, which is in accordance with Formula I, but has caused the rejection of most of the other formulas which we have constructed.

While our formula (I), as has been shown, explains most of the reactions already given, there is one serious objection to it. It represents a strong acid, and although our substance, when in alcoholic solution, gives an acid reaction with litmus,

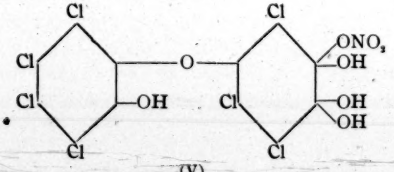
and dissolves in sodic hydroxide, and even sets free a little carbonic dioxide from acid sodic carbonate, it does not act on sodic, calcic, or baric carbonate in cold water. When boiled with baric carbonate and water, it seemed as if more carbonic dioxide was given off than when the substance alone was decomposed by boiling with water, but no barium went into solution. A possible explanation of this behavior with baric carbonate is that the substance was too slightly soluble in cold water to act upon it, and that, when hot, the barium salt was formed, but was immediately broken up by the boiling water with the formation of baric carbonate, a behavior in harmony with our knowledge of such salts. While this explains the action with baric carbonate fairly well, it does not show why the soluble sodic carbonate should be unaffected, when action is obtained on the one hand with sodic hydroxide and on the other with acid sodic carbonate. It must be confessed, therefore, that our substance behaves more like an acid phenol than like a carboxylic acid. We have tried to meet this serious objection to our formula (I) in two ways; (*A*) by bringing forward other properties of our substance, which point to the presence of a carboxyl group in it, and (*B*) by showing that other formulas are open to even greater objections.

A. Although most of the five-carbon ring hydroxy acids seem to give salts with ease, Zincke and Küster[1] have described two from which they were obtained with great difficulty; in fact, only the barium salt could be made, and this by the action of baric hydroxide on an alcoholic solution. No mention is made of experiments with carbonates, but this fact, coupled with the unusual way of preparing the barium salt, makes it seem probable that these two undoubted carboxyl acids behaved toward them abnormally, possibly like ours. The formation of our ester by the action of alcohol and sulphuric acid indicates the presence of a carboxyl acid, but it cannot be accepted as a proof, since there are many cases on record in which a phenol hydroxyl with negative environment is con-

[1] Ber. d. chem. Ges., **21**, 2719 (1888); **23**, 812 (1890).

verted into an alkoxyl under these conditions.[1] Hoffmann[2] gave as a proof of the presence of carboxyl in these cyclo-hydroxycarboxyl acids the fact that their esters were saponified by aqueous sodic hydroxide *in the cold*, since Salkowski[3] had found that even picryl ether must be boiled with alkali for a long time before it is decomposed. In applying this proof to our methyl compound no decisive result was obtained. It dissolved partially in cold sodic hydroxide, but the solution was not complete until it had been boiled, when a far-reaching decomposition took place. The fact that it dissolved at all, however, seems to us to point strongly to the presence of carboxyl. When our compound was heated to 100° with phosphoric pentachloride and oxychloride, hydrochloric acid was given off in large quantity, and after treatment with water to destroy the chlorides of phosphorus the unaltered substance was recovered. This certainly is most easily explained by the formation of an acid chloride converted again to the acid by water, whereas, if the acidity is caused by a phenol hydroxyl instead of a carboxyl, the original substance would not have been obtained. While no one of these observations gives an absolute proof of the existence of carboxyl in our substance, together they furnish a considerable body of evidence in favor of it.

B. If the acid properties are due to a phenol hydroxyl and not to a carboxyl, we can find no way of representing the substance except with two six-carbon rings; and the best formula of this sort we have found is (V).

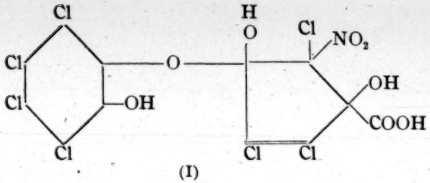


(V)

[1] For instance, Ber. d. chem. Ges., **17**, 2106 (1884); **21**, 603, 1900 (1888). Monats. Chem., **21**, 875 (1900). Ber. d. chem. Ges., **38**, 2864 (1905); **15**, 1427 (1882). Ann. Chem. (Liebig), **244**, 72 (1887). J. Chem. Soc., **77**, 3344 (1900). D. R. P., 173,730 (1906).

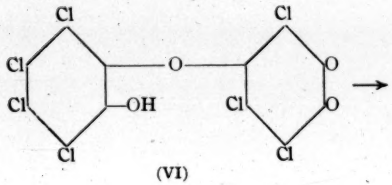
[2] Ber. d. chem. Ges., **22**, 1263 (1901).

[3] Ann. Chem. (Liebig), **174**, 259.

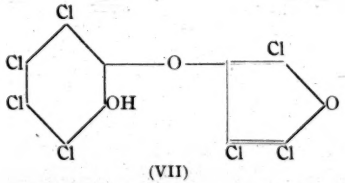


(I)

The most striking reaction studied by us was the conversion of the quino hemiether (VI) into the cycloketone (VII) by the action of nitric acid:



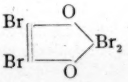
(VI)



(VII)

(giving the intermediate product I or V), followed by that of acetic anhydride. The formation of the cycloketone (VII) must be preceded by the formation of a five-carbon ring acid like (I), and the question arises, in what stage of the process is this acid formed? If by the nitric acid, (I) is the formula of the intermediate product; if by the acetic anhydride, (V) or some other similar formula represents the structure of this compound. When it is remembered that the conversion of the six-carbon into the five-carbon ring acid consists in adding water to the former, it is hardly conceivable that this change can have been brought about by acetic anhydride, in which

case no water can be obtained from outside, and although the molecule of (V) contains exactly the necessary amount of water, there seems no chance that it would take part in this reaction before it was removed by the acetic anhydride, which must convert $C(OH)_2$ into CO. This seems to us a conclusive argument against (V) and all other six-carbon ring formulas. On the other hand, the formation of (I) from (VI) by nitric acid is not without analogy, for, although such acids have usually been formed by the action of alkalies, Flint and one of us[1] obtained the compound



(VIII)

by the action of nitric acid and bromine on tetrabromorthoquinone, which must have been preceded by the formation of a five-carbon ring hydroxycarboxylic acid.[2]

Although the argument given above seems to us to disprove all six-carbon ring formulas, we add, by way of confirmation, a few properties of our substance, which agree with the view that it contains a five- rather than a six-carbon ring. Its very marked stability toward acids, and the ease with which alkalies act on it, recall at once the five-carbon cycloketone (VIII) of Flint and one of us, since these were among its most striking properties, and a similar stability toward acids has been observed by Hantzsch.[3] He has also obtained several six-carbon rings more or less modified by additions analogous to (V) and related formulas,[4] but they are easily converted again to the original aromatic or quino compound by a number of reactions, including reduction. Our substance is reduced only with a great deal of difficulty, and in no case have we observed a return to the quino body. This is the more striking

[1] THIS JOURNAL, **43**, 135 (1910).

[2] Compare also Zincke and Gerland [Ber. d. chem. Ges., **20**, 3216 (1887)] and Zincke and Küster [*Ibid.*, **21**, 2917 (1888); **23**, 812 (1890)] who obtained such acids by the action of boiling water.

[3] Ber. d. chem. Ges., **20**, 2780 (1887); **22**, 1238 (1889).

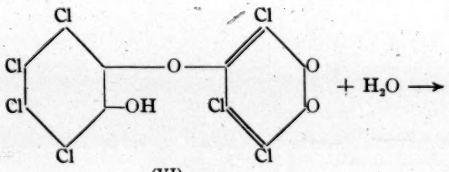
[4] Hantzsch: *Ibid.*, **21**, 2421 (1888).

because the red hexachlororthoquinopyrocatechin ether,

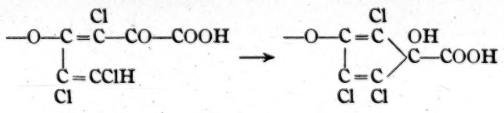
$$C_6Cl_4O_2C_6Cl_2O_2$$

has appeared with great frequency in our experiments with tetrachlororthoquinone and its derivatives. Its complete absence throughout our work with this substance can therefore be taken as evidence that the quino ring here undergoes a deep-seated transformation.

The formation of our substance from the hemiether (VI) is represented by the following sequence of formulas:

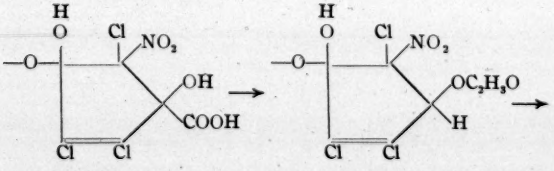


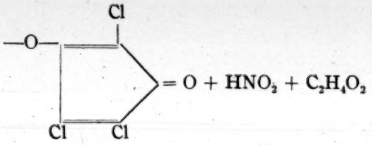
(VI)



followed, or preceded, by the addition of nitric acid to the upper double bond to give (I).

The mechanism of the reaction by which acetic anhydride converts the acid (I) to the cycloketone (IX) may perhaps be explained as follows: The acetic anhydride, in trying to force its way against the steric hindrances to the hydroxyl which is surrounded by so many radicals, drives out carbonic dioxide from the carboxyl:

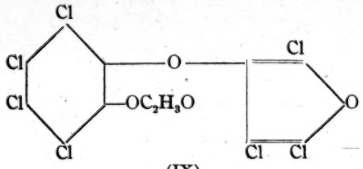




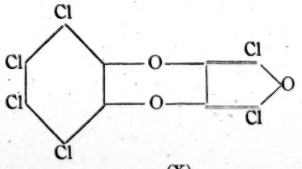
and the acetate of a secondary alcohol thus formed has such a tendency to be oxidized that it removes the nitric acid from the ring, and is converted by it into the ketone and acetic acid; or this last step may consist of a substitution followed by oxidation, as follows:

$$2 >CHOC_2H_3O + 2HNO_3 \longrightarrow 2 >CH(ONO_2) + 2C_2H_4O_2 \longrightarrow 2 >CO + N_2O_3 + H_2O$$

The formula of the cycloketone is (IX), and it is therefore



(IX)



(X)

the acetoxytetrachlorpyrocatechin hemiether of trichlorketocyclopentadiene.

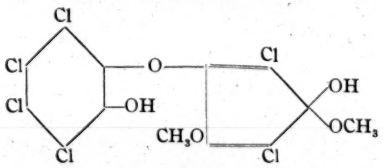
The acetyl group can be replaced by hydrogen by treatment with hydrochloric acid and alcohol. The original acetyl compound, or its hydroxyl derivative, if treated with pyridine, is converted into a vivid red compound (Formula X), therefore, the tetrachlorpyrocatechin ether of dichlorketocyclo-

pentadiene. That pyridine could remove acetyl chloride under such circumstances was shown by an experiment, in which it converted the acetyl hemiether,

$$C_6Cl_4(OC_2H_3O)OC_6Cl_3O_2$$

into the complete ether, $C_6Cl_4O_2C_6Cl_2O_2$. We found, however, to our surprise, that we could not get the complete ether from the benzoyl compound $C_6Cl_4(OC_7H_5O) - O - C_5Cl_3O$, by the action of pyridine.

The two complete ethers, (X) and $C_6Cl_4O_2C_6Cl_2O_2$, resemble each other very closely, which is a strong argument in favor of our formula. Thus, they are both vivid red,[1] whereas the corresponding hemiethers are but slightly colored; the melting points are very high; and they are very slightly soluble. Formula X is also supported by the fact that, when treated with sodic methylate in methyl alcohol, our ether-ketone takes up two molecules of methyl alcohol, forming, after acidification, the tetrachlorpyrocatechin hemiether of -hydroxy-1,4-dimethoxy-2,5-dichlorcyclopentadiene (XI), which is to be ex-



(XI)

pected, as our previous work has shown that hexachlororthoquinopyrocatechin ether, $C_6Cl_4O_2C_6Cl_2O_2$, takes up alcohols easily, forming alkoxyl hemiethers.

The fact that we did not succeed in preparing an oxime from this substance (X), or any of those related to it, does not tell against our formula, since a ketone containing so much chlorine would form an oxime with difficulty, if at all. When heated to 225°–240°, our red compound (X) turns white,

[1] This strong color may be connected with the symmetrical structure of these ethers, but further experiment is necessary before this explanation can be accepted.

and this change of color is accompanied by a loss of about 18 units of molecular weight. All our attempts to explain this behavior are mere guess work with our present knowledge, since the organic product was so unmanageable that we were unable to obtain any information about it with the amount at our disposal, because at the time we made this observation we could no longer prepare the red ether, although it had been obtained with ease in our earlier work. For this reason we have been obliged to leave our work on this compound in a decidedly unfinished state in other respects also.

By the action of nitric acid and glacial acetic acid on the hexachlormethoxyorthoquinopyrocatechin hemiether,

$$C_6Cl_4(OH)OC_6Cl_2(OCH_3)O_2$$

a substance was obtained which analyzed for

$$C_6Cl_4(OH)OC_5Cl_2(OCH_3)(NO_2)(OH)_2COOH$$

but it is doubtful whether it is related to the tetrachlorpyrocatechin hemiether of 2-nitro-2,4,5-trichlor-1,3-dihydroxycyclopentene-1-carboxylic acid (I), because with acetic anhydride it forms a monoacetyl compound, instead of undergoing the far-reaching decomposition to a cycloketone like this substance. The determination of its structure must be left for future work. Several compounds have been obtained in the course of this work which we could not study thoroughly. Provisional structural formulas for them in harmony with those already discussed will be found in the experimental part.

EXPERIMENTAL

Action of Nitric Acid on Heptachlororthobenzoquinopyrocatechin Hemiether

Twenty grams of the hemiether, $C_6Cl_4(OH)OC_6Cl_3O_2$, dissolved by the aid of gentle heat in enough glacial acetic acid to form a solution saturated at ordinary temperatures, were mixed with 5 cc. of fuming nitric acid (specific gravity 1.5), and, after the mixture had been warmed for 5 minutes to a temperature not above 65°, water was added to the warm solution until a slight permanent cloudiness had been formed, when on cooling a mass of crystals separated, or more commonly a red oil was deposited, which was converted into crys-

tals by stirring with a glass rod in contact with water; or, if it remained obstinately liquid, the crystals could usually be obtained by washing with successive portions of water followed by scratching with the glass rod. On diluting the mother liquor an additional fairly large amount of crystals was obtained. Earlier in our work the whole of the product was thrown down by an excess of water, but the subsequent purification was much more difficult in this case than in that just described, which was the result of a careful study of the conditions of the reaction. Even with the utmost care, however, the process failed occasionally.

The crystals obtained as described above were usually red, but most of the color was removed on washing by decantation with large quantities of water, after which they were collected, dried on a steam plate, powdered, and boiled with a mixture of 3 parts of benzene to one of ligroin, which dissolved out a troublesome viscous impurity without taking up much of the substance. The residue, freed from ligroin by drying, was dissolved in hot benzene, and precipitated by ligroin, when ill-defined crystals were obtained. In about 5 out of 30 or 40 preparations a product melting with decomposition between 159° and 165° was obtained, while in the remainder the product melted between 176° and 198°. In both cases the variation in the decomposition point caused by different conditions of heating was unusually large, so that this point was essentially of no value in determining the purity of the substance.

Compound Melting between 159° and 165°; Perhaps the Tetrachlorpyrocatechin Hemiether of the Nitrodichlorhydroxycyclopentadienecarboxylic Acid, $C_{12}H_3O_7NCl_6$.—We have not found the conditions on which the formation of this compound depended, and therefore obtained it only by accident, but, as it appeared chiefly in the earlier parts of the work, we should study the effect of slightly smaller amounts of nitric acid and precipitation of all the organic matter at once by water, if it were important enough to make it worth while to find out the conditions for its formation. It was purified by repeated crystallization from a mixture of benzene and

ligroin, and two different samples (I–IV and V–VI) were analyzed in the hope of proving it was a definite compound, as the decomposition point could not be used for this purpose.

I. 0.2747 gram substance, dried at 130°, gave 0.3090 gram CO_2 and 0.0440 gram H_2O.

II. 0.3945 gram substance gave 0.4409 gram CO_2 and 0.0546 gram H_2O.

III. 0.6285 gram substance gave 13.20 cc. moist N_2 at 15°.6 and 765 mm.

IV. 0.1166 gram substance gave 0.2094 gram AgCl.

V. 0.1087 gram substance dried at 80° gave 0.1962 gram AgCl.

VI. 0.1092 gram substance gave 0.1981 gram AgCl.

	Calculated for $C_{12}H_3O_7NCl_6$	Found I	II	III	IV	V	VI
C	29.63	30.68	30.48	...	...	...	...
H	0.62	1.78	1.54	...	...	...	...
N	2.88	...	...	2.47	...	...	...
Cl	43.85	...	...	...	44.38	44.62	44.85

The formula $C_6Cl_4(OH)—O—C_5Cl_2(OH)(NO_2)COOH$ may be provisionally assigned to this substance.

Properties of the Tetrachlorpyrocatechin Hemiether of the Nitrodichlorhydroxycyclopentadienecarboxylic Acid (?)—From alcohol and water, white or cream-colored flosslike crystals are obtained, while from benzene and ligroin crystals of rather an indefinite form are deposited. It melts with effervescence as low as 159°, if heated slowly, but by rapid heating it can be made to melt as high as 165°. It is soluble in all the common solvents, even in hot water, from which it is deposited in flocks; but it does not crystallize well from any of its solutions, the best solvent for it being a mixture of benzene and ligroin. The strong acids have no apparent action on it, but it is soluble in sodic or ammonic hydroxide with a pale yellow color. Owing to the small amount of material at our disposal, all these results must be considered preliminary.

Compound Melting between 176° and 198°. Tetrachlorpyrocatechin Hemiether of 2-Nitro-2,4,5-trichlor-1,3-dihydroxycyclopen-

tene-1-carboxylic Acid, $C_6Cl_4(OH)—O—C_5Cl_3(OH)_3(NO_2)COOH$. —In purifying this substance, which was the usual product of the reaction, we found differences of as much as 32° between the decomposition points of specimens purified in different ways. As these differences are to be ascribed in great part to the unusually strong influence of different conditions on the decomposition point, this property cannot be used as a criterion of purity. To take its place we have analyzed specimens purified in a number of different ways (*A*–*G*) with the results given below:

A. Purified by crystallization from benzene and ligroin followed by glacial acetic acid and water.

B. Crystallized from benzene and ligroin followed by methyl alcohol.

C. Crystallized from benzene and ligroin.

D. *C* recrystallized once from methyl alcohol and once from benzene and ligroin.

E. Crystallized once from each of the following solvents: benzene and ligroin, ethyl alcohol and water, methyl alcohol and water, benzene and ligroin.

F. Crystallized twice from each of the following solvents: benzene and ligroin, methyl alcohol, acetone, and finally once from benzene and ligroin.

G. Crystallized several times from glacial acetic acid and water.

	Melting point	Analyses
A	160°	Cl 46.00
B	176°	Cl 45.33, 45.62
C	181°–182°	Cl 45.82, 46.00; C 26.59; H 1.89
D	192°	Cl 45.66, 45.74; C 27.46; H 1.60
E	...	C 27.31, 27.01; H 1.21, 1.86; N 2.87
F	188°	Cl 45.96, 46.08
G	180°	Cl 46.11

The maximum differences between the determinations are 0.78 for chlorine and 0.88 for carbon, and therefore it is safe to infer that the substance is a definite compound, and pure or nearly so in all the cases. As the details of some of these analyses should be given, we have selected *E* (I–III)

and *F* (IV–V) as the most thoroughly purified specimens. They were dried at 94°.

I. 0.4746 gram substance gave 0.4752 gram CO_2 and 0.0517 gram H_2O.

II. 0.2644 gram substance gave 0.2618 gram CO_2 and 0.0441 gram H_2O.

III. 0.3113 gram substance gave 8.01 cc. moist N_2 at 22°.3 and 757 mm.

IV. 0.1297 gram substance gave 0.2411 gram AgCl.

V. 0.1165 gram substance gave 0.2171 gram AgCl.

	Calculated for $C_{12}H_4O_8NCl_7$	Found I	II	III	IV	V
C	26.74	27.31	27.01	....	...	...
H	0.74	1.21	1.86	....	...	...
N	2.59	...	...	2.87	...	...
Cl	46.15	...	...	....	45.96	46.08

Molecular-weight determinations by the boiling-point method:

VI. 0.6348 gram substance in 19.07 grams benzene, Δ = 0°.162, K = 26.70.

VII. 0.643 gram substance in 18.52 grams acetone,[1] Δ = 0°.117.

VIII. 3.109 grams substance in 17.28 grams acetone, Δ = 0°.600.

	Calculated for $C_{12}H_4O_8NCl_7$	Found VI	VII	VIII
Mol. wt.	538.5	549	512	517

These results indicate that the substance was formed by the addition of the elements of one molecule of nitric acid and one of water to the heptachlor hemiether, $C_6Cl_4(OH)OC_6Cl_3O_2$, and for reasons given in the introduction we have assigned to it provisionally the constitution represented by the following name:

Properties of the Tetrachlorpyrocatechin Hemiether of 2-Nitro-2,4,5-trichlor-1,3-dihydroxycyclopentene-1-carboxylic Acid.—The best formed crystals are obtained from methyl alcohol, and have a hexagonal shape with modifications, which could not

[1] K = 17.25. Jones: THIS JOURNAL, **31**, 114 (1899).

be identified on account of their small size, but there was always deposited from this solvent a viscous ring on the side of the dish even after many recrystallizations. From ethyl alcohol and water needles are obtained; from the other common solvents it is deposited in indefinite flakes, or as a viscous mass. The purest specimens were nearly white with a brownish tinge. It melts with effervescence at temperatures which are much influenced by the conditions of heating; the highest point obtained was 198° by dipping the tube into the hot bath, but by slow heating the same specimen could be made to melt at 176°. The gases given off during the melting contained carbonic dioxide, an oxide of nitrogen, hydrochloric acid, and water recognized by the usual tests. The loss in weight, when heated till constant between 195° and 200°, was studied quantitatively; six determinations gave the following percentages: 26.14, 26.02, 25.1, 24.3, 27.7, 26.72. The residues from the last two determinations contained 53.50 and 53.84 per cent. of chlorine; a loss of one molecule each of carbonic dioxide, hydrochloric acid, water and nitric dioxide would amount to 26.81 per cent., and a new substance formed by such a loss would contain 53.93 per cent. of chlorine. The residue was so unmanageable that we were unable to isolate any definite substance from it.

The nitro hemiether is freely soluble in alcohol, ether, acetone, or glacial acetic acid; moderately soluble in chloroform, tetrachloride of carbon, or benzene; nearly insoluble in ligroin or water.

When boiled with water it is slowly decomposed, yielding carbonic dioxide, recognized by the precipitate with baryta water; an oxide of nitrogen, detected by its action on diphenylamine dissolved in strong sulphuric acid; and tetrachlorpyrocatechin, recognized by its melting point, 194–195°, solubilities and reactions with ferric chloride and with nitric acid; there was also a considerable amount of tar, from which we could extract nothing further.

This decomposition by boiling water seems to be prevented by the presence of acetic acid, or hydrochloric acid. The substance is, in fact, remarkably stable toward acids, as speci-

mens heated on the steam bath for a whole day with sulphuric acid were recovered unaltered on dilution. Strong nitric acid, or hydrochloric acid, is without apparent action on it in the cold.

A solution of the substance in alcohol and water reddens litmus paper, and, if the powdered solid is dropped into a cold solution of acid sodic carbonate, there is a slight effervescence, but none could be obtained from neutral sodic carbonate or from calcic or baric carbonates in the cold. As already stated, it gives off carbonic dioxide, when boiled with water alone; but, if baric carbonate was also present, the evolution of gas seemed to be somewhat greater, and in one case clusters of white plates melting at 190° were obtained, but in too small quantity for study. No barium, however, could be detected in the solution. Cold sodic hydroxide dissolves it, but it is not reprecipitated by acids. On standing, the solution develops the characteristic purple color of chloranilic acid. On warming a solution of the substance in aqueous sodic hydroxide, fine black particles appeared in the liquid, which were filtered off, and yielded no definite compound. The filtrate, after acidification, gave a blue color with diphenylamine, and green with ferric chloride, so probably some oxide of nitrogen and some chlorpyrocatechin had been formed, but the ether extract from it, when evaporated to dryness on the steam bath, gave a viscous residue, which took fire spontaneously the first but not the second time we obtained it. Attempts were made to prepare the lead salt from a solution of the substance in acetone or methyl alcohol by adding sodic hydroxide till faintly alkaline, then a drop of acetic acid and plumbic acetate until a precipitate ceased to form (a special experiment had shown that a larger quantity of water than that contained in the plumbic acetate gave no precipitate with our solution). The precipitate was washed with acetone (or methyl alcohol) and water, and dried for analysis. Five specimens gave percentages of lead varying from 30.45 to 45.52 ($C_{12}H_2O_8NCl_7Pb$, Pb_2 7.84) so that it was evident we had not prepared a definite compound. This lead salt, treated with ethyl iodide either alone or with alcohol, benzene, or glacial

acetic acid, gave much plumbic iodide, but no organic substance could be isolated from the product.

A two per cent. solution of sodic methylate in methyl alcohol dissolved the substance in the cold, and the solution became straw-colored after a few minutes. On dilution with acidified water a precipitate was formed, which was identified as tetrachlorpyrocatechin, while the filtrate showed the characteristic color of chloranilic acid, and gave a test for an oxide of nitrogen with diphenylamine. Viscous substances were also observed, one yellow and soluble in benzene, the other red and insoluble, but they were so unpromising that they were not studied. Sodic ethylate seemed to cause a less extensive decomposition, but the products were no more satisfactory.

Pyridine produced no visible change in the cold with a solution of the compound in alcohol, or glacial acetic acid, but on warming the liquid turned dark, and a gas was given off. On adding water a pink or brown precipitate was thrown down, from which no crystals could be isolated. We have some reason to think that a better result might be obtained by carefully regulating the length of the heating. Phenylhydrazine, benzylphenylhydrazine, aniline and dimethylaniline gave an evolution of gas and similar black solutions in which no definite organic products could be found.

When a mixture of sodic acetate, glacial acetic acid and the substance was heated on the steam bath, carbonic dioxide and oxides of nitrogen were given off, whereas no such decomposition took place with glacial acetic acid alone. The solution contained much chloranilic acid, and a pale yellow substance crystallizing from methyl alcohol in long prisms melting after one crystallization at 170°, while there was suspended in it a white substance insoluble in the ordinary solvents, which blackened at 260°. Both these substances appeared in such small quantities that we did not attempt to investigate them. Argentic acetate, heated with a solution of our compound in glacial acetic acid, or methyl alcohol, gave two white products, one freely soluble in alcohol but insoluble in benzene, which melted at 180° after two crystallizations, but still contained traces

of silver; the other less soluble in alcohol, from which it could be obtained in needles, was free from silver and nitrogen. In practice the experiments did not seem so promising as in this account of them, and therefore were not continued.

The substance was moistened with phosphoric oxychloride covered with twice its weight of phosphoric pentachloride, and heated under a return condenser on the steam bath for three hours, when it liquefied, and gave off hydrochloric acid in quantity, but on pouring the cooled solution into water the unchanged substance was recovered, as it gave the characteristic hexagonal crystals from methyl alcohol and contained 45.78 per cent. of chlorine instead of the 46.15 per cent. required by the theory; melting point, 186°–188°. In another experiment phosphoric pentachloride alone was used, and the mixture was heated to 110°. In this case we did not succeed in freeing the unmanageable viscous product from phosphorus. Exactly the result which would be expected, if the hydroxyl had taken part in the reaction.

The substituted pyrocatechin cyclopentenehemiethercarboxylic acid offers a marked resistance to reducing agents; no action was observed with sulphurous dioxide with water, alcohol, or glacial acetic acid, or with zinc and hydrochloric acid; tin and hydrochloric acid turned the solid yellow, but the action was a superficial one, as most of the substance proved to be unchanged. Accordingly, the body was treated with glacial acetic acid mixed with an equal volume of strong hydrochloric acid and heated with tin on the steam bath. After an hour the solid had gone into solution, and the product was then precipitated with water acidified with hydrochloric acid. The white, viscous precipitate could not be made to crystallize, and after many efforts to purify it by precipitation the work was abandoned, as the results promised not to be worth the amount of time necessary to obtain them. The action of acetic anhydride, of acetyl chloride or of benzoyl chloride is described later.

Tetrachlorpyrocatechin Hemiether of 2-Nitro-2,4,5-trichlor-1,3-dihydroxycyclopentene-1-carboxylic Methyl Ester, $C_6Cl_4(OH)OC_5Cl_3(OH)_2(NO_2)COOCH_3$.—One gram of the acid

was dissolved in the least quantity of acetone and treated with a 1 : 5 solution of sodic hydroxide till strongly alkaline, when 5 cc. of dimethyl sulphate were added gradually with shaking and cooling. Afterward more of the sodic hydroxide was added, continuing the shaking and cooling until a precipitate appeared and the mixture had become permanently alkaline. After standing for half an hour, it was precipitated with water and enough hydrochloric acid to acidify it, and the precipitate was washed with water, dried, and recrystallized at first from alcohol and water, later from acetone containing a little ligroin, till it melted at 221°, when it was dried at 130°.

I. 0.1073 gram substance gave 0.1967 gram AgCl.

II. 0.1002 gram substance gave 0.1821 gram AgCl.

	Calculated for $C_{13}H_6O_2NCl_7$	Found	
		I	II
Cl	44.97	45.34	44.94

There was not enough of the substance for a combustion, and our later attempts to prepare it gave a different product, in which we succeeded in recognizing tetrachlorpyrocatechin by its crystalline form, solubilities, melting point, 194°–195°, and color with ferric chloride, and tetrachlorveratrol, detected by the melting point, 89°–90° instead of 88°, according to Brüggemann,[1] by its crystalline form, solubilities and volatility with steam, and confirmed by an analysis of a somewhat impure specimen, which gave results as near as could be expected. These later results were evidently due to the decomposition of the hemiether by the sodic hydroxide.

Properties of the Methyl Ester Melting at 221°.—It does not crystallize well from any common solvent, but the best result was given by acetone with a little ligroin, from which it was deposited in clusters of rather indefinite cream-white needles. It melts with effervescence at 221°, the gases formed giving a blue color with diphenylamine. It is soluble in all the common organic solvents except ligroin. Acids and alkalies produce no apparent change; occasionally the alkaline solutions gave a blue color with diphenylamine, but more commonly no reaction could be obtained.

[1] J. prakt. Chem., [2] **53**, 251.

Action of Sulphuric Acid and Methyl Alcohol on the Nitrohemiether

Tetrachlorpyrocatechin Hemiether of the 2-Nitro-2,4,5-trichlorcyclopentene-1,3-oxidecarboxylic Methyl Ester, $C_6Cl_4(OH)OC_5Cl_3O(NO_2)COOCH_3$.—This reaction was tried in the hope of finding an easier method for the preparation of the methyl ether just described, but, although a methyl group was introduced, a molecule of water was removed at the same time, giving the substance mentioned in the title. One part of the nitro hemiether was dissolved in 10 parts of methyl alcohol, and 20 of strong sulphuric acid were added slowly, when much heat was evolved. The mixture was then heated on the steam bath from 4 to 6 hours. During this time white crystalline flakes appeared, the quantity of which increased when the mixture was allowed to stand overnight. The solution was poured off, the crystals washed thoroughly with small portions of methyl alcohol, in which they are only slightly soluble, and then crystallized, at first from a mixture of benzene and ligroin, afterward from tetrachloride of carbon and ligroin, and dried for analysis.

I. 0.2501 gram substance gave 0.2675 gram CO_2 and 0.0259 gram H_2O.

II. 0.2172 gram substance gave 0.2308 gram CO_2 and 0.0228 gram H_2O.

III. 0.1076 gram substance gave 0.2020 gram AgCl.

IV. 0.1039 gram gave 0.1950 gram AgCl.

	Calculated for $C_{13}H_4O_7NCl_7$	Found			
		I	II	III	IV
C	29.18	29.17	28.98	...	...
H	0.75	1.16	1.17	...	...
Cl	46.49	...	...	46.42	46.39

Properties of the Tetrachlorpyrocatechin Hemiether of the 2-Nitro-2,4,5-trichlorcyclopentene-1,3-oxidecarboxylic Methyl Ester.—It crystallizes from tetrachloride of carbon in compact clusters of needles, from most of the other organic solvents in thin rhombic plates. It melts at temperatures between 221° and 228°, according to the speed of the heating, forming a colorless liquid and giving off gases which produce a blue

color with diphenylamine in strong sulphuric acid. It is easily soluble in benzene, chloroform, or tetrachloride of carbon; slightly soluble in alcohol, or ligroin. These solubilities, combined with its tendency to crystallize, make it easy to purify, in pleasing contrast to most of the related substances. The three strong acids are without apparent action on it. It dissolves slightly in a cold solution of an alkali, completely if warmed, giving an orange solution, which turns red on acidification, possibly from a trace of chloranilic acid, and deposits tetrachlorpyrocatechin, but these reactions do not appear always by any means. This alkaline solution gave a blue test with diphenylamine also only occasionally. Sodic methylate gave an unpromising viscous product.

Acetyl Derivative of the Methyl Ester, $C_6Cl_4(OC_2H_3O)OC_5Cl_3O(NO_2)COOCH_3$.—Five grams of the substance melting at 221°–228° described above were heated with twenty grams of acetyl chloride for two hours on the steam bath under a return condenser, the liquid was then evaporated off, the white residue washed with methyl alcohol, and purified by adding hot methyl alcohol to a hot benzene solution of the compound, when some crystals were precipitated at once, and the amount was increased as the liquid cooled. It melted at 189° and was dried at 120°.

I. 0.5639 gram substance gave 0.6538 gram CO_2.

II. 0.4155 gram substance gave 0.4813 gram CO_2 and 0.0467 gram H_2O.

III. 0.1515 gram substance gave 0.2637 gram AgCl.

IV. 0.1713 gram substance gave 0.3010 gram AgCl.

V. 0.7590 gram substance gave 20.08 cc. moist N_2 at 28° and 764.8 mm.

	Calculated for $C_{15}H_6O_8NCl_7$	Found I	II	III	IV	V
C	31.23	31.62	31.59	...	...	....
H	1.04	...	1.26	...	...	....
Cl	43.11	...	...	43.04	43.00	....
N	2.43	...	...	...	...	2.92

I. 0.5995 gram substance in 26.17 grams C_6H_6 gave Δ 0°.226.

II. 1.0999 grams substance in 26.17 grams C_6H_6 gave Δ 0°.418 by the freezing-point method; $K = 51.00$.

	Calculated for $C_{15}H_6O_8NCl_7$	Found I	Found II
Mol. wt.	576.5	517	513

Occasionally a substance melting at 224° was obtained instead of that analyzed, but we could not prepare enough of this for analysis; in one case the acetyl chloride left the substance unaltered.

Properties of Tetrachlorpyrocatechinacet Hemiether of 2-Nitro-2,4,5-trichlorcyclopentene-1,3-oxidecarboxylic Methyl Ester.—It crystallizes from benzene and alcohol in white rhombic prisms, which melt at 189° with effervescence to a straw-colored liquid. Easily soluble in benzene; slightly soluble in alcohol, ether, tetrachloride of carbon, glacial acetic acid, or ligroin; insoluble in water. Strong acids, or alkalies, produce no visible effect on it in the cold. The hydrochloride of hydroxylamine did not act on the substance, when heated with it in alcoholic solution. When the experiment was tried in presence of somewhat less than the calculated amount of sodic carbonate, the acetyl group was removed, leaving the methyl ether, shown by the melting point 226°–228°, and an analysis for chlorine which gave 46.09 per cent. instead of 46.49.

Tetrachlorpyrocatechinacet Hemiether of Trichlorketocyclopentadiene, $C_6Cl_4(OC_2H_3O)OC_5Cl_3O$.—Five grams of the nitro hemiether melting at 176°–198° were heated in an Erlenmeyer flask with 10 cc. of acetic anhydride on the steam bath for half an hour, when it was found that carbonic dioxide and an oxide of nitrogen were given off, the former recognized by its action with baric hydroxide, the latter by the appearance of a blue color in a solution of diphenylamine in sulphuric acid. The liquid was allowed to evaporate spontaneously, and the viscous residue was dissolved in its own volume of benzene, and upon dilution with three or four times its volume of alcohol deposited white scales. These, after washing with alcohol, were crystallized from a mixture of benzene and alcohol, until they showed the constant melting point 165°, when they were dried at 100° for analysis. Although the compound was only slightly soluble in alcohol, it was a difficult matter to free it from its viscous impurity. Acetyl chloride gave the same

results, but in this case the warming should take place under a return condenser.

I. 0.3166 gram substance gave 0.3840 gram CO_2 and 0.0271 gram H_2O.

II. 0.3632 gram substance gave 0.4427 gram CO_2 and 0.0278 gram H_2O.

III. 0.1744 gram substance gave 0.3699 gram AgCl.

IV. 0.1478 gram substance gave 0.3151 gram AgCl.

V. 0.1490 gram substance gave 0.3149 gram AgCl.

	Calculated for $C_{13}H_3O_4Cl_7$	Found				
		I	II	III	IV	V
C	33.09	33.08	33.24	...	...	...
H	0.64	0.96	0.85	...	...	...
Cl	52.70	...	...	52.44	52.71	52.25

III, IV and V were analyses of specimens from three different preparations, and these results were confirmed by another combustion and two other chlorine determinations.

I. 0.5290 gram substance in 21.20 grams C_6H_6 gave Δ 0°.275.

II. 0.9495 gram substance in 21.20 grams C_6H_6 gave Δ 0°.510 by the freezing-point method.

	Calculated for $C_{13}H_3O_4Cl_7$	Found	
		I	II
Mol. wt.	471.5	463	447

Properties of the Tetrachlorpyrocatechinacet Hemiether of Trichlorketocyclopentadiene.—It crystallizes from a mixture of benzene and alcohol in white glistening rhombic plates, which melt at 165°, although under special conditions a temperature as high as 168° was observed. Soluble in most of the common organic solvents; slightly soluble in ethyl or methyl alcohol or ligroin. Strong acids or alkalies have no visible action on it in the cold, but short heating on the steam bath with hydrochloric acid and alcohol gave ethyl acetate with a substance described later; and on one occasion after 20 hours tetrachlorpyrocatechin. Acetic anhydride has no further action on it, and none could be detected with hydroxylamine hydrochloride. Aniline, phenylhydrazine, or benzylphenylhydrazine, even when diluted with solvents, gave tarry products, from which no definite compounds could be isolated.

Its behavior with alcohol and hydrochloric acid or with pyridine is described later.

Tetrachlorpyrocatechin Ether of 2,5-Dichlor-1,1-diacetoxycyclopentadiene, $C_6Cl_4O_2C_5(OC_2H_3O)_2Cl_2O$(?)—The mother liquors left after the crystallization of the substance prepared by the action of acetic anhydride on the nitro hemiether yielded a viscous mass on evaporation, which could not be converted into a crystalline substance by treatment with any of the common solvents. It was, therefore, dissolved in benzene and treated with pyridine, which converted the ketocyclopentadiene hemiether into the red complete ether, and this crystallized out. The filtrate from these crystals, on evaporation, left a dark viscous residue, which was heated with acetic anhydride either with or without benzene, until it turned black, and became so thick as to flow slowly even when warm, after which, on cooling, it showed a tendency to crystallize. Accordingly it was dissolved in chloroform and excess of tetrachloride of carbon added, which precipitated the tar. When the supernatant liquid had become clear, it was decanted and the liquid tar treated again with tetrachloride of carbon; this last extract was filtered off, since the treatment had made the tar too viscous to pass through the paper. The solution, on slow evaporation, deposited white crystals, which were purified by crystallization from tetrachloride of carbon and alcohol, from benzene, and from benzene and alcohol, till they showed the melting point 188°, when they were dried at 80°.

I. 0.3095 gram substance gave 0.4101 gram CO_2 and 0.0574 gram H_2O.

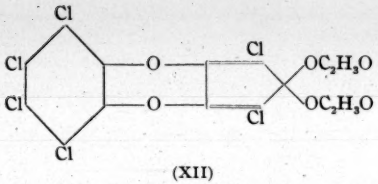
II. 0.2466 gram substance gave 0.3299 gram CO_2 and 0.0512 gram H_2O.

III. 0.1153 gram substance gave 0.2000 gram AgCl.

IV. 0.1122 gram substance gave 0.1940 gram AgCl.

	Calculated for $C_{12}H_8O_4Cl_6$	Found I	II	III	IV
C	36.36	36.14	36.49	...	...
H	1.21	2.07	2.32	...	...
Cl	43.03	...	...	42.89	42.75

Of the possible graphic formulas for this substance (XII)



(XII)

agrees best with the reactions by which it was formed, and has therefore been adopted provisionally for the purpose of indexing, but it is obvious that more work is necessary before it can be considered established. The substance is therefore the tetrachlorpyrocatechin ether of 2,5-dichlor-1,1-diacetoxy-cyclopentadiene.

Properties.—It crystallizes from a mixture of tetrachloride of carbon, or chloroform, with alcohol, in white hexagonal prisms, from benzene in long needles, from benzene and alcohol in rhombic plates. It melts at 188° to a colorless liquid; it is soluble in ether, acetone, chloroform, tetrachloride of carbon, or benzene; less soluble in alcohol or ligroin. It is not visibly affected by the three strong acids, or by alkalies even when warm.

When this compound, melting at 188°, was boiled for several hours with alcohol and an excess of hydroxylamine hydrochloride, the solid gradually went into solution. The straw-colored liquid thus obtained gave with water a white emulsion containing some brownish yellow crystals, the amount of which increased on standing. These were separated from an amorphous precipitate and crystallized from benzene and ligroin until they melted at 180°. Two analyses showed it was not pure, but that it contained over 10 per cent. more chlorine than the original compound. No test for nitrogen could be obtained after fusion with sodium, but such a negative result is not entitled to much weight. The substance seems to be the same with that melting at 180°–183° obtained in the same way from the ketone ether and described later.

Tetrachlorpyrocatechin Hemiether of Trichlorketocyclopenta-

diene, $C_6Cl_4(OH)OC_5Cl_3O$.—This compound was obtained by saponification of its acetyl compound (melting at 165°) already described, as follows: Two grams were heated with a mixture of 5 cc. of strong hydrochloric acid and 20 cc. of alcohol until the odor of ethyl acetate was no longer perceptible; then the solid, which showed no visible change, was purified by shaking with water and crystallization from benzene and alcohol, followed by benzene and ligroin. It melted, when dipped into the hot bath; at 188°, and was dried at 80°.

I. 0.1107 gram substance gave 0.2557 gram AgCl.

II. 0.1099 gram substance gave 0.2539 gram AgCl.

	Calculated for $C_{11}HO_3Cl_7$	Found I	Found II
Cl	57.86	57.13	57.43

Properties of the Tetrachlorpyrocatechin Hemiether of Trichlorketocyclopentadiene.—It crystallizes from benzene and alcohol in clusters of white needles and melts with decomposition at 182°–185°, if heated in the bath; at 188°, if dipped into the hot bath. It is freely soluble in most of the organic solvents; slightly soluble in methyl or ethyl alcohol, ether or ligroin. Strong acids or alkalies are without visible effect on it in the cold, but when heated for several hours with hydrochloric acid and alcohol, tetrachlorpyrocatechin was formed, recognized in the usual way. In spite of many attempts we did not succeed in isolating the other product of this reaction. Pyridine converts the hemiether into the red compound described in the next section, which it also forms with the acetyl body.

Tetrachlorpyrocatechin Ether of Dichlorketocyclopentadiene, $C_6Cl_4O_2C_5Cl_2O$.—This substance was obtained by the action of pyridine on a benzene solution of the corresponding heptachlor hemiether (melting at 188°), or its acetyl compound (melting at 165°). The viscous residue left after evaporation of the mother liquors obtained in purifying the last compound was an excellent source of this ether, and it first yielded us a good supply of the body, but later we failed in obtaining it in quantity, so that we were forced to leave some of our work in an unfinished condition. This is a good example of

the frequently occurring cases in this work, where processes failed to give the results obtained at first, although the conditions were kept as nearly identical as possible. When a benzene solution of one of the materials just mentioned was mixed with pyridine, the liquid darkened, then turned red, and soon bright red hexagonal plates appeared in considerable quantity. Occasionally a white product was also observed, but this disappeared on longer standing. The red crystals were purified by crystallization from benzene and alcohol, when they melted with decomposition at 264° to 272°, according to the conditions of heating. That the action in these cases consisted in the removal of hydrochloric acid or acetyl chloride by the pyridine was confirmed by studying its action on the hemiether, $C_6Cl_4(OH)OC_6Cl_3O_2$, and its acetyl compound, both of which were converted into the ether

$$C_6Cl_4O_2C_6Cl_2O_2$$

The substance melting from 264° to 272° gave the following results on analysis:

I. 0.1048 gram substance gave 0.2292 gram AgCl.
II. 0.1032 gram substance gave 0.2252 gram AgCl.
III. 0.1138 gram substance gave 0.2472 gram AgCl.

	Calculated for $C_6Cl_4O_2C_6Cl_2O$	Found I	Found II	Found III
Cl	54.19	54.08	54.12	53.71

III was prepared from the viscous residue and was known to be somewhat less pure than I and II.

Properties of the Tetrachlorpyrocatechin Ether of Dichlorketocyclopentadiene.—It crystallizes from a mixture of benzene and alcohol in very thin, bright red, hexagonal plates. The best way to obtain these is to dissolve the compound in benzene and add a quantity of alcohol, when the crystals are gradually deposited. If heated it loses color between 220° and 225°, becoming cream white, and then melts between 264° and 272°, according to the conditions of heating. The loss was determined between 225° and 240°.

I. 0.2310 gram substance lost 0.0107 gram.
II. 0.2167 gram lost 0.0100 gram.
III. 0.1352 gram lost 0.0064 gram.

	I	III	III
Loss	4.62	4.61	4.73

A loss of 18 units from the molecular weight amounts to 4.7 per cent.; but we are unable to explain the nature of this loss, as no pure compounds could be obtained from the residue, which evidently contained two products, one viscous and soluble, the other amorphous and insoluble in nearly all the common solvents. Unfortunately, our usual method of preparation failed to yield the red mother substance before we had finished the study of this reaction. The red compound is slightly soluble in the common organic solvents, more so in benzene than in the others, but not freely soluble in this. The strong acids and alkalies had no visible action on it.

Phenylhydrazine in somewhat dilute acetic acid once gave a substance crystallizing in square pyramids, but we were never able to obtain it again in spite of many attempts. When the finely powdered red compound suspended in alcohol was heated with an excess of hydroxylamine hydrochloride, it gradually went into solution, and as soon as this had happened the liquid was poured into water, which threw down an uninviting yellow precipitate, showing, however, some signs of crystals. This was purified by crystallization from benzene and ligroin, and finally from ligroin alone, which yielded ill-defined light brown crystals, softening at 178° and melting at 180°–182°. It was dried at 80°.

I. 0.2036 gram substance gave 0.2167 gram CO_2 and 0.0232 gram H_2O.

II. 0.1004 gram substance gave 0.2289 gram AgCl.

III. 0.1061 gram substance gave 0.2423 gram AgCl.

	Found		
	I	II	III
C	29.03	...	...
H	1.27	...	...
Cl	...	56.37	56.46

This substance seems to be the same as that obtained under similar conditions from the ether of the diacetoxycyclopentadiene. It cannot be the expected oxime, as that contains 52.20 per cent. of chlorine and 32.35 per cent. of carbon.

These results seem to indicate tetrachlorpyrocatechin, which contains 29.02 per cent. of carbon and 57.25 per cent. of chlorine and melts at 194°–195°, so our substance melting at 180°–182° might be an impure specimen of this substance; and this hypothesis is supported by the fact that it is turned red by nitric acid and that it is decidedly hard to purify tetrachlorpyrocatechin by crystallization from the solvents used by us.

Action of Sodic Methylate on the Tetrachlorpyrocatechin Ether of Dichlorketocyclopentadiene

Tetrachlorpyrocatechin Hemiether of the 1-Hydroxy-1,4-dimethoxydichlorcyclopentadiene, $C_5Cl_4(OH)OC_5Cl_2OH(OCH_3)_2$.—The red compound melting at 264°–266°, suspended in a little methyl alcohol, was treated with a two per cent. solution of sodic methylate in methyl alcohol until the green substance formed at first had gone into solution, when upon acidification with dilute hydrochloric acid, and further dilution with water, an orange-colored oil was deposited. This was washed with water and then scratched with a glass rod until it changed into a crystalline mass, which was washed with successive small portions of methyl alcohol to remove viscous matter, crystallized twice from benzene and ligroin, and once from methyl alcohol, when it melted at 180°, and as the amount was too small to permit further purification, it was dried at 70° for analysis.

I. 0.1023 gram substance gave 0.1944 gram AgCl.

II. 0.1028 gram substance gave 0.1943 gram AgCl.

	Calculated for $C_{11}O_3Cl_4.2CH_3OH$	Found I	Found II
Cl	46.61	46.99	46.73

The substance is therefore formed from the ketone ether by the addition of the elements of two molecules of methyl alcohol.

Properties of the Tetrachlorpyrocatechin Hemiether of the Hydroxydimethoxydichlorcyclopentadiene.—It crystallizes in white cubes from methyl alcohol and melts with decomposition between 175° and 180°, according to the conditions of heating. It is soluble in all the common organic solvents ex-

cept ligroin. The best solvent for it is a mixture of benzene and methyl alcohol. The strong acids have no visible action on it in the cold, but hot nitric acid converts it into a red oil; sodic hydroxide solution dissolves it without change of color, and it is thrown down from this solution as a colorless oil by hydrochloric acid.

Action of Sodic Ethylate on the Tetrachlorpyrocatechin Ether of Dichlorketocyclopentadiene

Tetrachlorpyrocatechin Hemiether of the Hydroxydiethoxydichlorcyclopentadiene, $C_6Cl_4(OH)OC_5Cl_2OH(OC_2H_5)_2$.—The ether was suspended in a little alcohol and a three per cent. solution of sodic ethylate added until the green precipitate formed at first dissolved, when hydrochloric acid and water were added to complete precipitation, and the pale yellow oil thrown down was washed with water. On adding a few drops of ethyl alcohol and scratching the oil with a rod it solidified, after which it was washed with small quantities of ethyl alcohol to remove the viscous matter, and then dissolved in hot alcohol, when, after adding hot water to the solution, until the first turbidity appeared, and scratching the dish with a glass rod as it cooled, needles were obtained. The yield was small, and owing to the difficulty of preparing the mother substance, the amount of material was enough for only two analyses, the first of which was made on a specimen dried for a day *in vacuo* after being air-dried. It melted at 93°.

0.1014 gram substance gave 0.1746 gram AgCl.

	Calculated for $C_{13}H_{12}O_5Cl_6.H_2O$	Found
Cl	42.34	42.57

The specimen for the second analysis was dried at 50°.

0.1074 gram substance gave 0.1933 gram AgCl.

	Calculated for $C_{13}H_{12}O_5Cl_6$	Found
Cl	43.92	44.50

It is to be regretted that we did not have material enough to determine whether the substance dried *in vacuo* really contained a molecule of water of crystallization. A certain con-

firmation of the single analysis is given by the fact that water was used in purifying it, and that the melting point is abnormally low, 93°, whereas the methyl compound melts at 180°. The whole of the substance was used in the second analysis so that no melting point could be taken with the substance dried at 50°.

Properties of the Tetrachlorpyrocatechin Hemiether of Hydroxydiethoxydichlorcyclopentadiene.—It crystallizes from ligroin in clusters of needles, from methyl alcohol in poorly defined cubes. It melts at 93° to a pale yellow liquid, which undergoes no visible change, even when the temperature is carried up to 200°. It is soluble in alcohol, ether or benzene; insoluble in water. It melted without change of color in hot hydrochloric acid, but in the cold no visible effect was produced by the three strong acids or by sodic hydroxide solution (difference from the methyl compound).

Action of Benzoyl Chloride on the Nitrohemiethercarboxylic Acid Melting at 176°–198°

Tetrachlorpyrocatechinbenzoyl Hemiether of Trichlorketocyclopentadiene, $C_4Cl_4(OCOC_6H_5)OC_5Cl_3O$.—This reaction could be carried on with benzoyl chloride alone or diluted with toluene, but the best results were obtained by using the Baumann-Schotten method as follows: The hemiether was dissolved in acetone, and after being rendered alkaline with aqueous sodic hydroxide, benzoyl chloride in excess was added. On warming, a yellow oil was deposited which was washed with water and treated with a little alcohol, when glistening white scales appeared. These were crystallized from benzene and alcohol until they showed the melting point 172°, when the substance was dried at 100°. I and II are analyses of one preparation, III and IV of another.

I. 0.2724 gram substance gave 0.4057 gram CO_2 and 0.0440 gram H_2O.

II. 0.1093 gram substance gave 0.2055 gram AgCl.

III. 0.1191 gram substance gave 0.2229 gram AgCl.

IV. 0.0665 gram substance gave 0.1243 gram AgCl.

	Calculated for $C_{18}H_5O_4Cl_7$	Found I	II	III	IV
C	40.49	40.62	...	...	...
H	0.94	1.81	...	...	...
Cl	46.58	...	46.49	46.27	46.20

The action, therefore, with benzoyl chloride is exactly analogous to that with acetyl chloride or acetic anhydride.

Properties of the Tetrachlor pyrocatechinbenzoyl Hemiether of Trichlorketocyclopentadiene.—It crystallizes from alcohol in glistening white scales, which melt at 172° to a colorless liquid. Easily soluble in benzene, much less soluble in alcohol or ligroin. The strong acids or alkalies have no apparent action on it; and the same is true of pyridine or alcohol and hydrochloric acid, so that this benzoyl compound is much more stable than the acetyl derivative, which was attacked by both of these reagents. Hydroxylamine hydrochloride seemed to react but the product was not studied.

As acetyl chloride, acetic anhydride or benzoyl chloride decomposed the tetrachlorpyrocatechin hemiether of 2-nitro-2,4,5-trichlor-1,3-dihydroxycylcopentene-1-carboxylic acid,

$$C_6Cl_4(OH)OC_5Cl_3(OH)_2(NO_2)COOH$$

and therefore gave no means of determining the number of hydroxyls it contained, we thought of trying other methods to reach the desired result, but could find none available, since Schryver's[1] method needs 2 or 3 grams of material, which could not be provided without more labor than it was worth, and Tschugaeff's[2] method gave incorrect results in trial experiments with the ether $C_6Cl_4(OH)OC_5Cl_3O_2$, so that it was obviously not worth while to try it on our substance.

Action of Nitric Acid on the Hexachlormethoxyorthobenzoquinopyrocatechin Hemiether

Tetrachlorpyrocatechin Hemiether of Nitrodichlormethoxydihydroxycyclopentenecarboxylic Acid, $C_6Cl_4(OH)OC_5Cl_2(OCH_3)(OH)_2(NO_2)COOH(?)$—A warm saturated solution of the hemiether in glacial acetic acid was treated

[1] J. Soc. Chem. Ind., **18,** 533 (1899).
[2] Ber. d. chem. Ges., **35,** 3912 (1902).

with three per cent. by volume of fuming nitric acid and the mixture kept at a temperature of 50° to 60° for three or four minutes, after which water was gradually added until the first permanent precipitate was formed, when, on cooling, the orange solution deposited a voluminous mass of crystalline scales. These were washed with a little water, dried at 60°, and crystallized first from benzene and methyl alcohol, later from benzene and ligroin. These solvents gave poorly defined crystals, but were more efficient than any others we could find. The purified substance melted at 202° to 208°, according to the conditions of heating. It was dried at 60°.

I. 0.1325 gram substance gave 0.2139 gram AgCl.

II. 0.1335 gram substance gave 0.2155 gram AgCl.

	Calculated for $C_{13}H_7O_9NCl_6$	Found	
		I	II
Cl	39.81	39.92	39.91

The reaction is therefore analogous to that with the heptachlor hemiether.

Properties of the Tetrachlorpyrocatechin Hemiether of Nitrodichlormethoxydihydroxycyclopentenecarboxylic Acid.—It forms ill-defined, pure white crystals which melt with decomposition at 202° or 208°, according to the speed with which they are heated. It is soluble in ethyl or methyl alcohol, ether, acetone, chloroform, or benzene; very slightly soluble in ligroin; essentially insoluble in water. The best solvents are benzene and ligroin, benzene and methyl alcohol, or methyl alcohol alone. The three strong acids have no visible action in the cold; sodic hydroxide solution dissolves it without change of color. It is much more easily purified than the corresponding heptachlor compound.

Action of Acetyl Chloride or Acetic Anhydride on the Methoxy Compound Melting at 202° to 208°.—When this substance was heated for one hour with several times its weight of acetyl chloride, hydrochloric acid was given off in quantity, in fact the evolution started even in the cold. The cooled solution was poured into a large volume of cold water, which precipitated a viscous material, and this, when kneaded under water, became granular, and after crystallization from benzene and

ligroin melted with effervescence at from 195° to 215°. Two chlorine determinations indicated that the substance was the original compound (40.02 and 39.98 instead of 39.81 per cent.), in spite of the difference in decomposition points. It seemed, therefore, that an acetyl compound had been formed which was afterward decomposed by the water.

In a second experiment a mixture of the methoxy compound and an excess of acetyl chloride was heated for 4 hours instead of one. The precipitate with water was dirty white, and after being rendered granular by kneading with water was crystallized from methyl alcohol till it was white and melted between 150° and 170° (I and II). What seemed to be the same product was obtained by heating the methoxy compound with 10 times its weight of acetic anhydride on the steam bath for half an hour. On cooling, it was treated with methyl alcohol and evaporated on the steam bath, after which it was crystallized from benzene and methyl alcohol till it was white and melted at 146° (this lower point is probably due to differences in the conditions of heating). It was dried at 60° (III and IV).

I. 0.2193 gram substance gave 0.2570 gram CO_2 and 0.0444 gram H_2O.

II. 0.1140 gram substance gave 0.1697 gram AgCl.

III. 0.1071 gram substance gave 0.1589 gram AgCl.

IV. 0.1134 gram substance gave 0.1681 gram AgCl.

	Calculated for $C_{13}H_9O_{10}NCl_6$	Found			
		I	II	III	IV
C	31.25	31.96	...	...	...
H	1.56	2.26	...	...	...
Cl	36.94	...	36.81	36.68	36.65

The reaction, therefore, has consisted in the introduction of one acetyl group without the deep-seated decomposition observed during the similar treatment of the corresponding heptachlor hemiether.

Properties of the Tetrachlorpyrocatechinacet Hemiether of Nitrodichlormethoxydihydroxycyclopentenecarboxylic Acid.—It crystallizes from benzene and alcohol in clusters of white needles, from hot methyl alcohol in plates. When heated rapidly it

usually melts at 146° with decomposition, but if heated for some time at 110°, it is converted into another substance, which does not melt below 190°. A specimen heated to 105° for fifteen hours lost 7.7 per cent.; it was then accidently overheated, so that the residue could not be studied, and it was not certain that the loss was constant. This would amount to a loss of 44 units from the molecular weight. The acetyl compound is soluble in acetone, chloroform, tetrachloride of carbon or benzene; less soluble in methyl alcohol; essentially insoluble in water. With the three strong acids, or sodic hydroxide, no visible action is observed in the cold.

Methyl alcohol and sulphuric acid heated with the methoxy compound for 15 minutes had little action upon it, most of the original substance being recovered unchanged. We regret that lack of time prevented us from repeating the experiment with longer heating, as oxides of nitrogen began to come off toward the end of the 15 minutes.

Action of Nitric Acid on Hexachlorethoxyorthobenzoquinopyrocatechin Hemiether.—The ethoxy compound,

$$C_6Cl_4(OH)OC_6Cl_2(OC_2H_5)O_2$$

was dissolved in the least quantity of hot glacial acetic acid and the solution cooled to about 60° and treated with from 3 to 5 per cent., by volume, of fuming nitric acid. The mixture was kept at about 60° for five minutes, and then hot water was added until a slight turbidity appeared, after which, on cooling, a voluminous white precipitate was thrown down, and this was washed with water. A second compound, described later, was obtained from the filtrate and wash waters. The precipitate, after drying at 50°, was crystallized from benzene and ligroin, until it melted at 214°–215°, when it was dried at 70°. Analysis I was made with one preparation, II and III with another.

I. 0.1063 gram substance gave 0.1730 gram AgCl.
II. 0.1079 gram substance gave 0.1736 gram AgCl.
III. 0.1177 gram substance gave 0.1911 gram AgCl.

	Calculated for $C_6Cl_3(OH)OC_6Cl_2(OC_2H_5)O_2.HNO_3$	Found I	Found II	Found III
Cl	40.19	40.24	39.78	40.15

In the absence of sufficient data for assigning a structural formula to this substance it may be called the mononitric acid compound of the tetrachlorpyrocatechin hemiether of ethoxydichlororthoquinone.

Properties.—It separates from glacial acetic acid and water in glistening white scales; from benzene and ligroin in rhombic prisms; from tetrachloride of carbon in rhombic plates; thus, unlike the related compounds, it forms well defined crystals. It melts with effervescence at 210° or 215°, according to the speed with which it is heated. It is soluble in alcohol, ether, chloroform, tetrachloride of carbon or benzene; slightly soluble in ligroin; essentially insoluble in water. The strong acids have no apparent action on it in the cold; sodic hydroxide solution dissolves it, and acids give an oily precipitate with this solution; ammonic hydroxide dissolves it less easily, forming a yellow solution.

Dinitric Acid Compound of the Tetrachlorpyrocatechin Hemiether of Ethoxydichlororthoquinone.—The filtrate and wash waters from the preparation of the compound just described were mixed and allowed to stand, when white rhombic crystals in small amount were deposited, which were analyzed without further purification.

I. 0.1060 gram substance gave 0.1544 gram AgCl.

II. 0.1076 gram substance gave 0.1577 gram AgCl.

	Calculated for $C_6Cl_4(OH).O.(C_2H_5O)C_6Cl_2O_2(HNO_3)_2$	Found I	Found II
Cl	35.91	36.02	36.24

Although these results agree very well with the formula given, it is obvious that more analytical data are necessary before it can be accepted definitely.

The substance crystallizes from dilute acetic acid in white rhombic prisms, which when dipped into the hot bath melt at 145° with effervescence; if heated in the bath it softens at 130°, but then does not melt completely until 158°. It is soluble in alcohol, ether, chloroform, tetrachloride of carbon or benzene; slightly soluble in ligroin; essentially insoluble in water. The strong acids produce no visible change in the cold; sodic hydroxide dissolves it partially, but without change of color.

CAMBRIDGE, MASS.
March 14, 1913

ON THE REACTIONS OF BOTH THE IONS AND THE NONIONIZED FORMS OF ELECTROLYTES

THE REACTIONS OF SODIUM PHENOLATE WITH METHYL IODIDE AND ETHYL IODIDE IN ABSOLUTE ETHYL ALCOHOL AT 25° AND 35°

By H. C. Robertson, Jr., and S. F. Acree

[SEVENTEENTH[1] COMMUNICATION ON CATALYSIS]

(We are indebted to the Carnegie Institution of Washington for aid in these researches.)

In 1905 Brunel and Acree began an investigation to learn whether in all ordinary, and catalyzed, chemical reactions involving electrolytes (acids, bases and salts) the ions as well as the nonionized forms are concerned. The fundamental investigations of Arrhenius[2] and Ostwald[3] and their students had placed the ionization theory on a sound footing, but had, perhaps unfortunately, also led chemists, with a few exceptions,[4] to believe that the *ions* are the only portions of electrolytes capable of entering into transformations.[5] The very

[1] This Journal, **27**, 118; **28**, 370; **31**, 185; **32**, 606; **37**, 71, 361; **38**, 1, 258, 489, 746; **39**, 124, 145, 226, 300; **41**, 457, 483; **42**, 115; **43**, 358, 505; **44**, 219; **48**, 352; **49**, 116, 345, 369. Ber. d. chem. Ges., **33**, 1520; **35**, 553; **36**, 3139; **37**, 184, 618; **41**, 3199. Science, **30**, 617 (1909). J. Am. Chem. Soc., **30**, 1755. Dr. Robertson did this work in 1909 and 1910 and presented it as a dissertation for the Ph.D. degree in June, 1910. A few notes have been added by one of us to bring the work up to date, but the fundamental conclusions have not been changed.—S. F. A.

[2] Z. physik. Chem., **1**, 110, 631; **2**, 284; **4**, 226; **28**, 217, 326.

[3] J. prakt. Chem., [2] **27**, 1; **28**, 449; **29**, 406; **30**, 231; **31**, 307; **33**, 352; **35**, 112. Z. physik. Chem., **2**, 36, 136, 270.

[4] See especially Kahlenberg: J. Phys. Chem., **5**, 339; **6**, 1. Michael: This Journal, **43**, 322. Stieglitz: Cong. Arts and Sciences, St. Louis, 1904, and later papers. Acree: This Journal, **37**, 410; **38**, 258, and later papers.

[5] In recent years the application of these quantitative ideas to organic reactions has been used very successfully by a number of workers. In front rank stands the work of Stieglitz (This Journal, **39**, 29, 166, 402, 437, 586, 719. J. Am. Chem. Soc., **32**, 221; **34**, 1687. Congress Arts and Sciences, St. Louis, 1904) on the imido esters and their salts and his proof that the ions and nonionized substances are active. Especially important was his correlation of this work with the general problems of catalysis. Bredig (Z. Elektrochem., **9**, 118; **10**, 586; **11**, 528; **18**, 535, 539. Z. physik. Chem., **47**, 185) made a number of studies which he interpreted as reactions of ions, the best of which were perhaps his study of the catalysis of hydrogen peroxide by iodide ions, and of the decomposition of diazoacetic ester by hydrogen ions. The relation of this to the catalysis of esters through the activity of complex oxonium salts was discussed by him. Goldschmidt's work (Z. Elektrochem, **15**, 6. Z. physik. Chem., **60**, 728; **70**, 627; **81**, 30. Ber. d. chem. Ges., **39**, 711) on the esterification of organic acids

brilliancy of the new idea, together with the *apparent* evidence, and the authority of Arrhenius and Ostwald, dazzled chemists to such an extent that the possible activity of the nonionized substances was almost entirely neglected. When we began our work there was already some evidence that both the ions *and the nonionized forms* of acids, bases and salts are concerned in the well-known saponification of esters by acids and alkalies, in the inversion of cane sugar by acids, in the decomposition of diacetone alcohol by alkalies, in the formation of benzoin from benzaldehyde by potassium cyanide, in the inversion of menthone by sodium ethylate, in the rearrangement of acetylchloroaminobenzene by acids through the activity of the nonionized salt,

$$CH_3CONHClAnC_6H_5 \text{ (An = Cl, Br)}$$

and other cases discussed[1] in previous articles. All of these reactions had been assumed by others to involve only the hydrogen ions of the acid, the hydroxyl ions of the bases, or similar mechanisms.

The experimental evidence in all of these cases being in such condition that it could not be analyzed with absolute certainty, and the important factor of "salt catalysis" being so little understood, we deemed it wise to undertake the study of some typical organic reactions *in absolute ethyl alcohol* in order to measure all of the necessary factors with as high a degree of precision as possible. Ethyl alcohol was chosen as the solvent because in it the per cent. of ionization of different substances *varies far more* than in water, when the solutions are diluted from N/1 to N/2048. This fact is of the very greatest importance in studying the activity of the *nonionized electrolytes*, because *in N/1 alcoholic solutions, for instance, the concentration of the nonionized electrolyte is several times that found in the corresponding aqueous solutions, and the ac-*

in absolute ethyl alcohol proved the same general ideas and has formed, on account of its wealth of detail, one of our most important chapters. The work of Lapworth (J. Chem. Soc., **93**, 2163, 2203; **97**, 21; **99**, 1417, 2224; **101**, 2249; **103**, 252) on the influence of small amounts of water on esterification, conductivities, electromotive forces, and vapor pressures has formed one of our most brilliant chapters, because it furnished a much needed and far-reaching coördination of the physical properties and chemical activity of solutions, an example which should be followed by all chemists.

[1] For references see THIS JOURNAL, **48**, 352; **49**, 348.

tivity of the nonionized electrolyte is therefore easily measured in most cases studied by us.

We chose a few typical organic reactions for study, in some of which an electrolyte, for example an ethylate, was involved *purely catalytically* and was not decomposed during the chemical transformations, but in others of which the electrolyte was completely transformed into the end products. Such widely different cases were chosen to allow us to see whether the mechanism of the reaction is the same in both cases, both ions and nonionized electrolytes being involved alike in both classes of reactions. Our study of the *pure catalysis* of the reversible reaction

$$NaOC_2H_5 + RC : N + C_2H_5OH \rightleftharpoons NaOC_2H_5 + RC(:NH)OC_2H_5$$

by sodium, potassium and lithium ethylates, in which the ethylates are not changed into the end products, has shown that the mechanism of this reaction is essentially the same as that involving the sodium, potassium and lithium ethylates and methyl iodide or ethyl iodide, in which, of course, the ethylate is transformed into the end products:

$$C_2H_5ONa + IC_2H_5 \longrightarrow (C_2H_5)_2O + NaI$$

The evidence shows that the ethylates react in both cases through their ethylate ions as well as through their nonionized forms.

Another class of reactions studied by us and described in part in the present communication, and which have been found to be quite analogous to those involving ethylates and alkyl halides, are the changes involved when alkyl halides react with sodium, potassium and lithium phenolates in absolute ethyl alcohol:

$$C_6H_5ONa + ICH_3 \longrightarrow NaI + C_6H_5OCH_3$$

$$C_6H_5\bar{O} + ICH_3 \longrightarrow \bar{I} + C_6H_5OCH_3$$

The reactions proceed smoothly at 25° and 35° and the constants remain very regular throughout a large part of the transformation. The constants become from 3 to 5 per cent.

smaller toward the end of the change, probably because some of the alkyl halide may escape through the stoppers closing the flasks containing the reaction mixture, because the ether and sodium halides formed in the reaction suppress the ionization of sodium phenolate slightly, because there is probably a slight catalysis by the sodium halide formed, and especially because a small amount of the alkyl halide may form an olefin by a monomolecular reaction.[1] We have, therefore, disregarded at present the small decrease in the constants toward the end of the reaction and have considered the apparent course of the main reaction, which certainly seems to be bimolecular. We shall, however, study especially the side reaction involving the formation of olefins, along with the others.

In developing the equations[2] which we should use we may consider the case first in which the alkyl halide reacts with the phenolate anion. If these unite to form a complex anion in very *small traces*[3] and we represent the concentrations by the formulas, the equation

$$(a)\quad CH_3I \times \overline{An} = K \times \overline{CH_3I.An}$$

holds *approximately* for any given concentrations even though the value of the "stability constant" K is not constant for all concentrations. We cannot experimentally[4] measure K at present and our only reason for thinking that K should remain constant for all concentrations is that the stability constants of most complex salts, such as double cyanides, complex ammonium salts, etc., are fairly constant. If this complex

[1] Brussoff (Z. physik Chem., **34,** 129) found that ethyl iodide and potassium hydroxide in ethyl alcohol at 78° form 16 per cent. of ethylene.

[2] The K_i and K_m used here may be the sum or product of other constants and may be made to include "salt effects" of ions or molecules; the "salt effect," however, seems fortunately to be small in this case.

Since it has been shown by Carrara (Gazz. chim. ital., **26,** I, 119; **33,** I, 241. Ahren's Sammluing, **12,** 403. Lapworth and Partington: J. Chem. Soc., **99,** 1417) that the ionic mobilities of sodium, potassium and lithium salts hardly change with concentration we shall assume, until our further work is completed, that $\alpha = \mu_v/\mu_\infty$ and that $\alpha(A - x)$ represents the ionic concentration of the sodium phenolate or sod um ethylate.

[3] For the development of these equations see Johnson and Acree: THIS JOURNAL, **37,** 410; **38,** 258; **43,** 519; **48,** 352. Ber. d. chem. Ges., **41,** 3210, par. 1 and footnote 1, and p. 3214, par. 2, and other articles.

[4] We have planned some experiments to measure K.

yields the end products the following equations hold approximately, whether the complex salt is formed slowly (either reversibly or irreversibly) and decomposes rapidly, or is formed rapidly reversibly and decomposes slowly:

$$(b)\quad dx/dt = K'_i \times CH_3I.An = K'_i/K \times CH_3I \times An = K_i \times CH_3I \times An$$

But this is exactly the same equation that we get if the alkyl halide and anion react directly without the formation of an intermediate complex anion. In the one case our reaction velocity constant K'_i/K is the quotient of two constants, both of which (or the quotient) are assumed to be constant for all concentrations; in the other case we make no assumptions other than the constancy of the reaction velocity K_i.

In the present studies, however, the above equation fails to represent the entire reaction, and we may therefore consider the possibility of reactions of nonionized substances. It might well be that the *nonionized* double salt $C_2H_5I.NaOC_6H_5$ can decompose *in solution* into sodium iodide and phenyl ethyl ether just as Scholl[1] and Steinkopf have shown the *solid* (and presumably *nonionized*) cyanomethyl iodide-silver nitrate double compound to yield silver iodide and cyanomethyl nitrate. We may consider this nonionized double salt to be formed by the union of the alkyl halide with the anions and cations of the sodium phenolate, or by the union of the alkyl halide and nonionized sodium phenolate. These two processes are represented as follows:

$$(c)\quad C_2H_5I \times \overline{O}C_6H_5 \times \overset{+}{N}a = K' \times C_2H_5I.NaOC_6H_5$$

and

$$(d)\quad C_2H_5I \times NaOC_6H_5 = K'' \times C_2H_5I.NaOC_6H_5$$

It is clear that if sodium phenolate obeyed Ostwald's dilution law, and the equation

$$\overset{+}{N}a \times \overline{O}C_6H_5 = K''' \times C_6H_5ONa = \frac{K'}{K''} \times C_6H_5ONa$$

were true for all concentrations, K' and K'' also being constant,

[1] Ber. d. chem. Ges., **39**, 4393. Hantzsch and Caldwell: *Ibid.*, **39**, 2472. Acree and Loy: THIS JOURNAL, **45**, 224.

we could not possibly tell which of these two processes is taking place. The reaction (*c*) would be written

$$(e)\quad dx/dt = K_m \times C_2H_5I.NaOC_6H_5$$
$$= K_m/K'C_2H_5I \times OC_6H_5 \times Na$$
$$= \frac{K_mK''}{K'} \times C_2H_5I \times NaOC_6H_5 =$$
$$\frac{K_m}{K''} \times C_2H_5I \times NaOC_6H_5$$

Equation (*e*) also represents the catalysis, by the sodium ions, of the reaction between the alkyl halide and the phenolate ions.

The reaction (*d*) would be written

$$(f)\quad dx/dt = K_m \times C_2H_5I.NaOC_6H_5$$
$$= \frac{K_m}{K''} \times C_2H_5I \times NaOC_6H_5$$

which would also hold even if no complex salt were formed as an intermediate product. If the sodium phenolate obeyed the Ostwald dilution law these two equations could be used interchangeably and we could not know whether the sodium phenolate reacts through the sodium and phenolate ions together, or through its nonionized portion, or through both processes together, and we could not know whether a *negligible trace* of the complex salt is an intermediate product.

Sodium phenolate apparently does not obey Ostwald's dilution law and these equations (*e*) and (*f*) are not identical by any means. If Equations (*b*) and (*c*) represent the true reactions the total reaction can be represented by the Equation (*g*) if α is the ionization and $(A - x)$ is the concentration of the sodium phenolate, and $(B - x)$ is the concentration of the alkyl halide at time t and $x = 0$ when $t = 0$.

$$dx/dt = K_i\alpha(A - x)(B - x) + K_m\frac{\alpha^2}{V}(A - x)(B - x)$$
$$= \left[K_i\alpha + K_m\frac{\alpha^2}{V}\right](A - x)(B - x), \text{ or}$$
$$(g)\quad K_V = \left[K_i\alpha + K_m\frac{\alpha^2}{V}\right]/V = \frac{B}{t(A - B)}\ln\frac{B(A - x)}{A(B - x)}$$

The Equation (*h*) holds if Equations (*b*) and (*f*) represent the two side reactions:

$$(h)\quad dx/dt = K_i\alpha(A-x)(B-x) + K_m(1-\alpha)(A-x)(B-x)$$
$$= [K_i\alpha + K_m(1-\alpha)](A-x)(B-x), \text{ or}$$
$$K_V = [K_i\alpha + K_m(1-\alpha)]/V = \frac{B}{t(A-B)} \ln \frac{B(A-x)}{A(B-x)}$$
$$= \frac{x}{t(A-x)}$$

when the concentrations of the sodium phenolate and alkyl halide are equal. Therefore

$$VK_V = K_N = K_i\alpha + K_m(1-\alpha)$$

for normal solutions of ionization α when $1/V$ is the concentration of the sodium phenolate.

It may be stated at once that Equation (*g*) has led to satisfactory constants in only two cases, those of the reactions between methyl iodide and sodium ethylate and potassium ethylate, whereas Equation (*h*) gives satisfactory constants in all of the cases studied up to this time. Whether in those two particular cases the methyl iodide does react with both ions together, perhaps along with the nonionized molecules, or whether it is an arithmetical accident cannot be said at present. Since some other hypotheses have not yielded satisfactory constants we shall confine ourselves at present to the discussion of Equation (*h*).

It is evident, then, that when the reaction velocities and ionic concentrations are measured in various solutions we have variations in K_N, α, $(1-\alpha)$, A and B. We can therefore determine the values of K_i and K *for normal solutions* from the series of simultaneous equations,

$$K_N = K_i\alpha + K_m(1-\alpha)$$
$$K'_N = K_i\alpha' + K_m(1-\alpha')$$
$$K''_N = K_i\alpha'' + K_m(1-\alpha''), \text{ etc.}$$

which are obtained by equating the values of K_N observed against the corresponding values of $K_i\alpha + K_m(1-\alpha)$, and substituting the proper values in Robertson's equations,

$$K_m = \frac{K_N\alpha' - K'_N\alpha}{\alpha' - \alpha}$$

and

$$K_i = \frac{K'_N(1-\alpha) - K_N(1-\alpha')}{\alpha' - \alpha}$$

These two equations make it clear at once that K_m becomes zero when K_N is proportional to the ionic concentration of the salt. That is, if

$$K'_N : K_N = \alpha' : \alpha \quad \text{or} \quad K'_N\alpha - \alpha' K_N = 0$$

then

$$K_m = \frac{K_N\alpha' - K'_N\alpha}{\alpha' - \alpha} = \frac{0}{\alpha' - \alpha}$$

Similarly, K_i becomes zero when K_N is proportional to the molecular concentration of the salt $(1-\alpha)$. That is, if

$$K'_N : K_N = (1-\alpha') : (1-\alpha)$$

then

$$K'_N(1-\alpha) - K_N(1-\alpha') = 0$$

and

$$K_i = \frac{K'_N(1-\alpha) - K_N(1-\alpha')}{\alpha' - \alpha} = \frac{0}{\alpha' - \alpha}$$

Similarly, if $K_m = K_i$, then it follows that $K_N = K'_N$ and the velocity of the reaction, when referred to normal solutions, will not change with change in concentration.[1] In this case we find that $K_i = K_m = K_N$.

When we determine experimentally, with accuracy, the values of K_i and K_m by using two solutions of different concentrations we can calculate the reaction velocity at any other concentration. Smaller errors are involved when these two concentrations differ as widely as is experimentally advisable, the difference $\alpha' - \alpha$, etc., being then larger and smaller errors appearing in K_i and K_m. It is seen in Table XXVI that when N/1 and N/32 solutions are compared the values 0.0283 and 0.00476 are obtained for K_i and K_m, respectively, the average of all the values being 0.0282 and 0.00474. This agreement is excellent, but no better than was obtained in all the other work with other phenolates, and with sodium, potassium and lithium ethylates to be reported in another article.

[1] This case is approached closely in certain cases involved in the catalytic inversion of menthone by sodium ethylate, and the addition of alcohol to nitriles in the presence of sodium, potassium, lithium and tetramethylammonium ethylates, on which we shall report soon.

All the possible combinations have been used in determining K_i and K_m and the results are given in Tables XXVI and XL for methyl iodide at 25° and 35°, and Tables LIII and LXIV for ethyl iodide at 25° and 35°. As can be seen, the variation in the values obtained for K_i and K_m is considerable, those for K_i in Table XXVI varying between 0.0264 and 0.0300 and those for K_m varying between 0.000372 and 0.00574 in the case of the reactions with methyl iodide at 25°, and those for K_i and K_m at 35° varying in a similar manner. This variation of about 50 per cent., in some cases, in the values of K_i and K_m may seem to indicate a very large experimental error in the determination of the reaction velocity, K_N, or the per cent. of ionization, α, of the phenolate salt, but such is not the case; the form of the equations, in which small differences, $\alpha' - \alpha$, etc., appear, is really responsible for such apparently large errors. The following example will illustrate the point: In Table XXV we find the values 0.01272 and 0.01447 for K_N for N/8 and N/16 solutions of sodium phenolate and methyl iodide at 25°. These values give 0.00574 as the value of K_m in Table XXVI. But if the values 0.01259 and 0.01462 had been used for K_N, the first being *decreased* therefore only 1.00 per cent. and the second being *increased* only 1.00 per cent., the value 0.00449 would have been found for K_m, which is *22 per cent. smaller* than the value 0.00574 actually obtained. It is perfectly apparent, then, that in this phenolate work, in which K_i is about six times as large as K_m, very small errors in K_N and α appear greatly magnified in the variations of K_i and K_m. In the work on the sodium ethylate, however, in which $K_i = 2.13\ K_m$ for methyl iodide, an error of one per cent. in K_N makes an error of only about 10 per cent. in K_m. For that reason there is much less variation in the individual values of K_i and K_m for sodium ethylate and methyl iodide, as can be seen in another article dealing with these substances.

It is best, therefore, to use (1) the average of *all* the values obtained for K_i and K_m, or (2) the average of the more accurate *starred* values obtained in those equations in which

$\alpha' - \alpha$ is larger, or (3) to combine all the simultaneous equations into one having the form

$$K_N + K'_N + K''_N + \ldots . =$$
$$K_i(\alpha + \alpha' + \alpha'' \ldots .) + K_m(1 - \alpha + 1 - \alpha' + 1 - \alpha'' + \ldots)$$

with which the individual equations are compared to get the values of K_i and K_m, and call these the closest approximation to the *true values*. It is seen in Table XXVI that the values obtained for K_i and K_m by these different methods all agree very closely. The values obtained for K_i and K in Tables XXVI, XL, LIII and LXIV were averaged and the average values substituted in the equation $K_N = K_i\alpha + K_m(1 - \alpha)$. In this way "calculated" values for K_N at every concentration were obtained and these are compared with the "found" values of K_N in Tables XXVII, XLI, LIV and LXV. It will be seen that the calculated and observed values are fairly concordant, agreeing almost within the limit of experimental error. This agreement is seen to be satisfactory when we recall that in these reactions in which the K_i is much greater than K_m small errors in the measurement of K_N cause great variations in the other two constants.

It is seen from Tables XXVI, XL, LIII and LXIV that sodium phenolate reacts with methyl iodide and ethyl iodide at 25° and 35° in a way that accords with the above equations. The values obtained for methyl iodide are $K_i = 0.0282$ and $K_m = 0.00474$ at 25° and $K_i = 0.091$ and $K_m = 0.0131$ at 35°, while the data for ethyl iodide are $K_i = 0.0056$ and $K_m = 0.00099$ at 25° and $K_i = 0.0184$ and $K_m = 0.00323$ at 35°.

If this theory is correct all phenolates should react with methyl and ethyl iodides in such a way that *the same value for K_i, after it is freed of all disturbing physical and "salt" effects, should be obtained for unit concentrations of a given alkyl halide and the phenolate ion, whatever its source, whereas different values could be found for K_m, the activity of the alkyl halide and the nonionized phenolate salt.* The nonionized sodium, potassium and lithium phenolates are *different substances* and can therefore *react with different velocities* with

methyl iodide or ethyl iodide. Now the best evidence for the validity of this theory is that the application of these equations to the data obtained by the use of all three of these phenolates gives us *nearly the same values* for K_i but *different values* for K_m.

Mr. J. H. Shrader has completed a series of investigations on potassium and lithium phenolates at 25° and 35° and finds values for K_i and K_m for methyl iodide and ethyl iodide which accord excellently with our data. A résumé of all the constants is given here:

Methyl Iodide and Different Phenolates at 25°

		K_i	K_m
Dr. Robertson	Sodium phenolate	0.0282	0.0047
Mr. Shrader	Potassium phenolate	0.0283	0.0037
Mr. Shrader	Lithium phenolate	0.0289	0.0039

Methyl Iodide and Sodium Phenolate at 35°

		K_i	K_m
Dr. Robertson	Sodium phenolate	0.091	0.0131

Ethyl Iodide and Different Phenolates at 25°

		K_i	K_m
Dr. Robertson	Sodium phenolate	0.0056	0.00099
Mr. Shrader	Potassium phenolate	0.0052	0.00101
Mr. Shrader	Lithium phenolate	0.00534	0.00091

Ethyl Iodide and Different Phenolates at 35°

		K_i	K_m
Dr. Robertson	Sodium phenolate	0.0184	0.00323
Mr. Shrader	Potassium phenolate	0.0197	0.00270
Mr. Shrader	Lithium phenolate	0.0174	0.00319

When all of the data are analyzed carefully, and we consider the possibility of an "abnormal salt effect," and the fact that the results were obtained by two different workers, with different samples of materials, and different apparatus, and we remember especially the fact that relatively small experimental errors in K_N make large differences in K_i and K_m, as discussed on page 482, we see that the corresponding values for K_i agree well within the experimental errors. The values

for K_m vary considerably in many cases, in accordance with the theory. As we pointed out before, all of our work on the action of ethyl bromide, ethyl iodide and methyl iodide on sodium, potassium and lithium ethylates and on sodium phenyl-3-thiourazole harmonizes with the above experimental results and theory. We shall publish the details of all these investigations as quickly as possible.

The Study of Salt Catalysis

There is only one further point that needs discussion. It is seen from the foregoing pages that the reactions of sodium phenolate are not purely ionic, this transformation of the ions proceeding side by side with another involving, we believe, the nonionized salt. This deviation has been explained by Spohr[1] and Arrhenius,[2] and later by Lunden,[3] Euler,[4] Stieglitz,[5] and perhaps others, as an "auto effect" of the salt on the solvent or solution. We do not agree entirely with these workers and have explained our "salt catalysis" as due *chiefly* to the activity of the *nonionized salts* (the "normal" effect), augmented by a small "abnormal salt catalysis" resulting from changes in the physical properties of the solutions, and perhaps due partly to double compounds and to some role which electrons play. We are studying the question of "normal" and "abnormal" "salt catalysis" in connection with all these reactions, and we shall report our work later in detail when we study the reactions in concentrations varying from N/1 out to N/2048, especially in the presence of added salts. If there is an "abnormal salt effect" produced by the reacting phenolates, or metallic halides formed during the transformation, and such an effect can be analyzed by the equations

$$dx/dt = [1 + (f)C_{salt}][K_i\alpha + K_m(1-\alpha)](C_{salt}-x)(C_{alkyl\ halide}-x)$$

in which $(f)C_{salt}$ is a function of the total salt (or its ions) as

[1] J. prakt. Chem., [2] **33**, 32; **33**, 265. Z. physik Chem., **2**, 194.
[2] *Ibid.*, **1**, 110; **4**, 226; **31**, 197.
[3] *Ibid.*, **49**, 195.
[4] *Ibid.*, **52**, 348. Ber. d. chem. Ges., **39**, 2726.
[5] *Loc. cit.*

expressed first by Spohr, Arrhenius and others, the correction of K_i and K_m for $(f)C_{salt}$ must be either negligible in *nearly all* of the above reactions or have the same general order of magnitude for all three salts and the same alkyl halide. Even if the latter is the case, no surprise should be occasioned if we remember the fact that the physical properties of the corresponding solutions of all the salts concerned are very much alike.

We should lay especial stress on the fact that we have obtained results from our study of "salt catalysis" in both *concentrated* and *dilute*, or *ideal*, *solutions* which make entirely insufficient all theories proposed hitherto to explain the peculiar effect which some neutral salts have on some reactions, but not on others. We prefer, therefore, to reserve for the future our final discussion of salt catalysis, and define later the actual form of the expression $(f)C_{salt}$ used above.

EXPERIMENTAL

Introduction

Conrad and Brückner[1] have already studied the reactions of sodium phenolate with alkyl halides, but their work with these compounds was not very extensive. The methods used by them in their study of reaction velocities have been somewhat modified in details which seemed to involve sources of error. These investigators, having made up solutions of phenolates and of alkyl halides of the desired strength, mixed their entire solutions at one time in a large flask and, at the expiration of the desired time-period, pipetted out portions and titrated these. This procedure necessitated opening the flask containing the reaction-mixture a number of times and produced a loss of the volatile alkyl halide, particularly at the relatively high temperatures. It has seemed preferable to vary this procedure and carry out each individual reaction in a separate small flask of a capacity only slightly larger than the volume of solution to be introduced. In this way possible loss of alkyl halide by volatilization is avoided.

Solutions of sodium phenolate were made up as follows: A

[1] Z. physik. Chem., **3**, 450; **4**, 273, 631; **5**, 289; **7**, 274, 283.

solution of sodium ethylate having twice the strength desired for the sodium phenolate was prepared by removing the crust from sodium under ligroin, removing the ligroin by dipping small pieces into alcohol a few seconds, and then dissolving this clean sodium in absolute alcohol at 0° in a graduated flask. After the solution was brought to the proper temperature, the proper titrations with standard acid and methyl orange, and the necessary dilution with absolute alcohol, gave the solution of desired strength. A solution of similar concentration of dry phenol in alcohol was also prepared. By mixing equal volumes of the two solutions, a solution of sodium phenolate of the desired strength was obtained. The contraction on mixing the two solutions is very small, but any decrease in volume may be made up for by diluting to the mark of the flask with alcohol, if a calibrated measuring flask is used to receive the mixed solutions.

Conrad and Brückner, in studying the reactions of phenolates, made up their solutions in a similar way. They assumed, however, that when sodium ethylate is mixed with its molecular equivalent of phenol, the reaction takes place as below:

$$C_2H_5ONa + C_6H_5OH \rightleftarrows C_6H_5ONa + C_2H_5OH$$

and that the reverse reaction is inappreciable.

It was found, however, in the present investigation, that such is probably not the case.[1] On mixing equivalents of sodium ethylate and phenol, solutions of sodium phenolate were obtained which did not give satisfactory constants when reacting with alkyl halides. There was a steady though slight decline in the reaction velocity even in short time-periods. Tables I and II illustrate this fact. The logical conclusion is that not all of the sodium ethylate has been converted into phenolate, and that we have the two substances reacting at the same time with the alkyl halide. Since the velocity con-

[1] The variation of the per cent. of alcoholysis with the change in concentration has not been studied carefully enough to allow us to make these slight corrections in the work reported here. This subject is being investigated as fully as possible. Mr. Shrader has already made a study of the velocity of reaction of methyl iodide with mixtures of sodium phenolate and sodium ethylate, the latter, of course, because of its higher ionization, suppressing the alcoholysis of the sodium phenolate more effectively than does the phenol.

stant of sodium ethylate is about three times that of the phenolate, it disappears more rapidly. This would account for the decrease observed. The phenol liberated suppresses largely the further alcoholysis of the phenolate, and the constants for the longer time-periods are about the same as those obtained when 1 or 2 per cent. excess of phenol was present in the original phenolate solution.

It was found that on the addition of an excess of phenol better constants were obtained. This is noticeable when only 1 per cent. excess is added (Tables XIII and XIV). On comparing these values, however, with those in which no excess of phenol is used, we see that the former are somewhat lower in numerical value. This led to the addition of more phenol and it was found that the decrease in the velocity constant was very great when large quantities of phenol were added. Tables I to X and XIII and XIV show the effects obtained by the addition of from 1 per cent. to 30 per cent. excess of phenol.

A study of the rise in boiling point caused by the addition of varying excesses of phenol to a normal solution of sodium phenolate in absolute alcohol has been made. This should throw light on the subject by showing whether or not there is a double salt formation when an excess of phenol is added to the solution of sodium phenolate. It was found that there was no appreciable amount of double salt present at the boiling temperature of the solution since the rise of boiling point was nearly proportional to the molecular excess added. It is possible that some double salt might be present at the temperatures at which the reactions were carried out and that this is almost completely broken down at the boiling temperature. The question will be investigated further. A study of the change in viscosity, caused by the addition of varying excesses of phenol, must be made before any explanation of the phenomenon can be attempted.

In Table XI we have given figures to show the relation between the velocity of reaction and the excess of phenol. The data are derived from Tables I to X and XIII and XIV, on the assumption that one per cent. of free phenol lowers the reaction velocity about 0.75 per cent. These values are all

for 0.5 N solutions of sodium phenolate and methyl iodide at 25°.

It seems that, in preparing solutions of sodium phenolate as described above, it is necessary to add at least a slight excess of phenol in order to convert all the sodium ethylate into phenolate. *In all our reactions we have therefore added an excess of one per cent. over the calculated quantity of phenol.* It is seen from Tables I and XV that the numerical values of the velocity constants are only slightly and consistently lowered by the addition of this small excess. We shall consider this subject again in our reports on the reactions in very dilute solutions.

Probable Causes for the Decrease in Velocity Constants as the Reactions near Completion

In practically all the reactions of the alkyl halides that have been studied it has been found that there is a steady, though slight, decrease in the velocity constants as the reaction progresses. It is seldom possible to obtain concordant values after fifty per cent. of the reacting substances have undergone change. It will be seen from our tables that we have relied mainly on the first half of the reactions for the best constants. The cause of this decrease in velocity constants has been attributed by many investigators to a loss of alkyl halide during the course of the reaction. The question has been taken up in the present investigation and it is certain that only a small part of this decrease can be attributed to the above source.

Solutions of methyl iodide (this being one of the most volatile alkyl halides used) were used for a study of the question. Standard solutions were prepared by weighing into a measuring flask nearly full of absolute alcohol a slight excess over the calculated amount of methyl iodide. The volume of alcohol necessary to bring the solution to the desired strength was then added from a pipette, both solution and alcohol, of course, being at the correct temperature.

A normal solution of methyl iodide was prepared as above and two 10 cc. portions were withdrawn *by suction with an ordinary pipette.* Each of these was added to an aqueous solu-

tion of silver nitrate in a tube which was at once sealed and heated at 60° for 24 hours. The results of these analyses showed that about one per cent. of the alkyl halide had been lost in the process of making up and transferring the solutions.

These results were confirmed by other analyses, in some cases the loss of methyl iodide being even larger. It should be stated that the alkyl halide had been previously analyzed and was undoubtedly quite pure.

From these experiments it was realized that unless precautions were taken to eliminate the error involved by loss of alkyl halide, the velocity constants in long time-periods might be seriously affected. A special form of pipette has been therefore devised which has proved itself invaluable in working with the alkyl halides and volatile liquids and gases in general. Fig. I shows in detail the construction and mechanism of this apparatus, which is mounted on a suitable brass frame (*F*), and held in position by plaster of Paris in the small, raised, hollow, brass boxes (*S*).

The 10 cc. or 20 cc. pipette (*A*) is surrounded by a jacket (*B*) through which water from the constant temperature bath is made to circulate by a Brown and Sharp rotary pump. The solution to be measured out is contained in the flask (*R*), which, together with the wash-bulbs (*W*), is immersed in the constant temperature bath. A two-valve blowing bulb is attached at (*G*). The wash-bulbs (*W*) are filled with a small quantity of the solution to be measured out, in order that the air going through them may be saturated with the alcohol and alkyl halide, and hence not take up any from the solution in (*R*) and cause a decrease in the concentration of the alkyl halide solution contained therein. The bulbs (*C*) catch any solution that may be accidentally forced from (*A*). If a compressed air system is at hand the bulbs (*C*) can be half filled with mercury, which is then forced up and down by the air under pressure. In this way the same air is always kept in (*A*) and the left bulb (*C*) and is always saturated.

To fill the pipette, stopcock (*N*) is turned so as to connect (*A*) with (*R*), and the three-way stopcock (*M*) is turned so as to furnish an outlet from (*A*) to the air. On pressing the

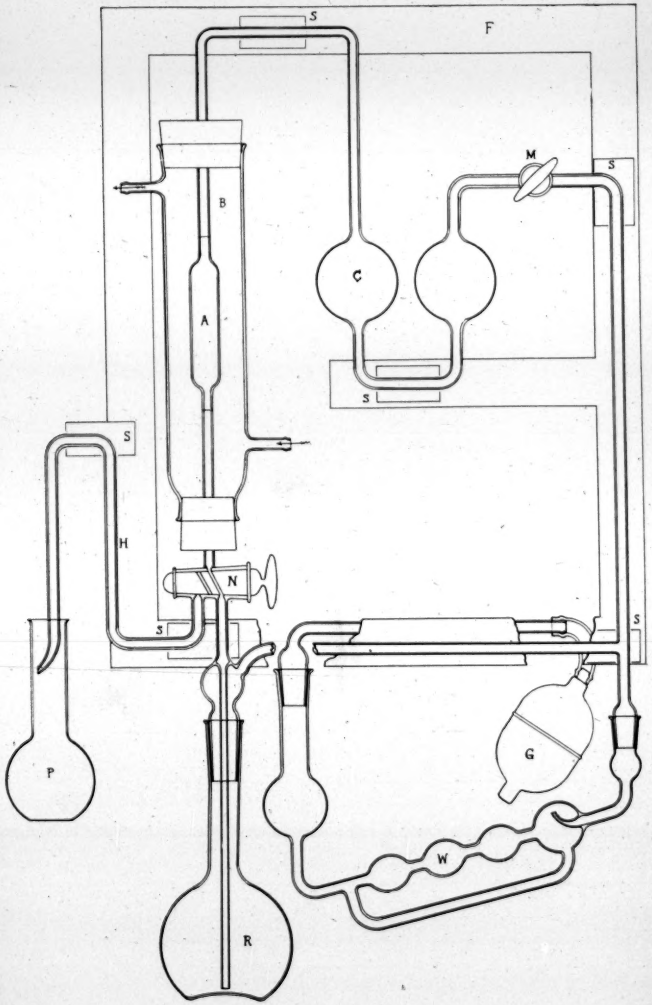


Fig. 1

blowing bulb (*G*), the solution in (*R*) is forced into the pipette (*A*), the air which reaches the solution in (*R*) being saturated with the vapors of the alkyl halide and alcohol by passage through the wash-bulb (*W*). To deliver the pipette, stopcock (*M*) is turned so as to connect (*A*) with (*G*), (*W*) and (*R*). Stopcock (*N*) is turned so as to connect (*A*) with the capillary outflow tube (*H*). The liquid flows into the flask (*P*), the tip of the outflow tube (H) being held just under the surface of the sodium phenolate solution already in (*P*), and the pipette (*A*) is at the same time filled with the air which is already compressed in (*R*) and saturated with the vapor of the alkyl halide. The flasks (*P*) containing the sodium phenolate solutions are brought to the correct temperature in the bath before the alkyl halide solution is added, are kept at the right temperature in a beaker of water from the bath during the transfer of the alkyl halide, and are immediately closed with cork stoppers. The necks of the flasks are covered with "rubber fingers" to keep out water, and the flasks are then *shaken in the bath* to give the solutions perfect homogeneity and the correct temperature. When the capillary outflow tube (*H*) is well covered with binding tape or other insulating material there is no great difficulty in mixing the solutions at the desired temperature, 0°, 25° or 35°. This apparatus has been of great service in the work with alkyl iodides, solutions of ammonia, methylamine and other volatile substances. When it is used, the loss from volatilization is much less than is occasioned by the use of an ordinary pipette. We give the analyses which were made of three 10 cc. portions of methyl iodide measured out by the aid of the above device, many others having been made by Loy and Miss Brown. The alkyl halide solution was 0.3 per cent. stronger than normal.

Analyses	Percentage normal found	Percentage normal calculated
1	100.21	100.30
2	100.12	100.30
3	100.05	100.30

It is evident that the loss of methyl iodide involved when the apparatus described above is used is only 0.1 to 0.3 per

cent., which is much less than that incurred with the ordinary form of pipette, namely, about 1 per cent. Loy[1] has found that only about 0.1 per cent. of ethyl iodide is lost from N or 0.1 N solutions used in this apparatus. We have therefore always made the solutions of methyl iodide and ethyl bromide 0.3 per cent. too strong, and the solutions of ethyl iodide 0.1 per cent. too concentrated.

Experiments were carried out to determine whether alkyl halide is lost from the reaction flasks after they are stoppered and placed in the constant temperature baths. It was found that their weight did not decrease perceptibly even after standing a week. If alkyl halide escapes, we must assume that the same amount of water vapor enters through the stoppers, which is very improbable.

It is evident that the decrease in velocity constants noticed as the time-periods become longer cannot be attributed solely to loss of alkyl halide. At present it seems most probable that it is mainly due to a monomolecular side-reaction in which an olefin (or ether) is formed, because Brussoff[2] found that ethyl iodide and potassium hydroxide in ethyl alcohol at 78° give about 16 per cent. of the theoretical amount of ethylene. Since Brussoff did not exercise the very greatest care in freeing the olefins from the ethers formed simultaneously, we may consider this 16 per cent. a maximum amount at that temperature. There is certainly much less formed at lower temperatures; our own experiments show that there is a smaller decrease in the constants at 0° than at 25°. Furthermore, Johnson has carried out a large number of alkylations of the salts of urazoles at 60° in acetone, methyl alcohol and ethyl alcohol and has found evidence that the olefin formation is considerable, although not as much as 5 per cent. even when the reactions were 85 per cent. completed. In Johnson's work there was liberated one molecule of urazole acid for each molecule of olefin formed, according to the equation:

$$C_2H_5I + NaUr \longrightarrow C_2H_4 + NaI + UrH$$

and he was able to titrate this urazole acid with standard alkali,

[1] Loy: Dissertation, Johns Hopkins University, 1910.
[2] Z. physik. Chem., **34**, 129.

and hence calculate the amount of olefin formed. When this was done he was able to make a correction in his data and show that the velocity of the alkylation of the urazole salt was practically constant throughout. We cannot do this, however, in our work on the alkylation of phenolates and ethylates because the acids liberated, phenol and ethyl alcohol, are too weak to be titrated. We are therefore carrying out experiments to measure the amount of olefin formed, and shall then make the proper corrections in our data. We are, furthermore, studying the alkylations of the salts of urazoles and other fairly strong acids in absolute alcohol, and in this case we shall be able to study the amount of this side reaction by measuring the amount of urazole or other acid set free. We have evidence now that, notwithstanding the fact that added ether accelerates the reaction velocity, a small amount of the decrease in the velocity constant is due to the slight suppression of the ionization of the sodium phenolate by the sodium halide and ether formed in the reaction. The sodium phenolate and alkyl halides used, and the ethers and halide salts formed, change slightly the physical constants of the medium; the effects of solvation and viscosity on the ionic and molecular migration velocities, per cent. of ionization and reaction velocities will, therefore, be considered, but these effects seem to be counterbalanced in the present studies in such a way that the values for K_i and K_m are approximately the same for the concentrated as for the dilute solutions.

The amount of the decrease in the velocity constant is not over 3 to 5 per cent. even when the reaction is 75 per cent. complete, and in the first half of the reaction is hardly more than the unavoidable experimental errors. We have therefore disregarded this decrease in the present articles and shall leave the further study of this point to the last refinement of our researches along these lines.

Preparation[1] *of Absolute Ethyl Alcohol*

With the exception of a few series of reactions carried out to determine the effect of traces of water on reaction velocity,

[1] We have been aided in this work on alcohol by a grant from the C. M. Warren Fund.

the solvent used was invariably nearly absolute alcohol. The work of numerous investigators[1] has shown that the effect of water on the velocity of reactions of this type may be a very important factor, and one that must be considered if accurate measurements are to be made. While the effect of traces of water on reactions between sodium phenolate and alkyl halides is not so great as in some other cases, it is nevertheless quite appreciable, and it seemed advisable to eliminate this factor by the use of solvents as free from moisture as it was practicable to obtain them. The dehydration of ethyl alcohol is a comparatively simple matter. The best commercial article was boiled several days with 400 grams of calcium oxide per liter of alcohol. After distillation, the treatment with calcium oxide was repeated, using a smaller proportion than before. The last traces of moisture were often removed by digesting the alcohol with turnings of metallic calcium and calcium oxide at 40°. At this temperature the metal is only slowly acted upon by alcohol, and the dehydration is very effective. After the first portion of calcium has passed into solution, second and third portions of about 10 grams or less per liter may be added and allowed to react at a moderate temperature. Such treatment will always be found sufficient to produce alcohol of a high degree of dehydration. We have used calcium oxide and calcium simultaneously because we found that metallic calcium alone increases the specific gravity when boiled some time with the alcohol. The increase in specific gravity is probably due to a catalytic decomposition of the alcohol into water and ethylene (or ether), which escapes. A sample of alcohol which had increased in specific gravity an amount corresponding to 0.18 per cent. water when treated with calcium was boiled with calcium oxide and was then found to contain only 0.03 per cent. of water. Our best samples of alcohol have been obtained by the use of calcium oxide alone. We have found calcium carbide to be very effective in a short time. We shall report soon in another arti-

[1] Acree: THIS JOURNAL, **41**, 457. Reid: *Ibid.*, **41**, 483. Goldschmidt and Sunde: Ber. d. chem. Ges., **39**, 711, and *loc. cit.* Joseph Gyr: *Ibid.*, **41**, 4322. Lapworth: J. Chem. Soc., **93**, 2163; *Loc. cit.* Bredig: *Loc. cit.* Biochem. *Z.*, **6**, 308. Ber. d. chem. Ges., **39**, 1756.

cle on some special apparatus and the methods found useful in preparing large quantities of pure alcohol.

Before the treatment with metallic calcium as above, the alcohol was invariably digested with 10 grams of silver nitrate or 3 grams of *m*-phenylenediamine hydrochloride per liter and distilled, after which it gave no decided tests for aldehydes.

It was found, in general, that the first treatment with calcium oxide gave alcohol of about 99.7 per cent. A second similar treatment in some cases gave alcohol of 99.99 per cent. purity. This was, however, only attained after several days' digestion at boiling temperature. It is much more convenient to remove the last traces of moisture with metallic calcium and calcium oxide.

It appears at present that specific gravity determinations made with a carefully calibrated pycnometer of at least 40 cc. capacity give the surest evidence of the dehydration of alcohol. The critical temperature of solution in kerosene, advocated by some investigators,[1] is hardly applicable as a test for absolute quantities of water, though it is certainly of great value in determining relative proportions. There is, necessarily, considerable variation, both in composition and dryness, between different samples of kerosene, and both factors are of essential importance. It was found that alcohol of specific gravity 0.78510 $\frac{25°}{4°}$, when mixed in equal volumes with a certain sample of commercial kerosene which had not been dried or distilled, gave a C. T. S. of 4°.02. With equal volumes of the same kerosene dried with calcium chloride and distilled the C. S. T. was —4°. Andrews suggests that kerosene used for this purpose be first treated by passing steam through it for a time to free it from its most volatile constituents and then dried and used. We have found that the C. T. S. of alcohol in kerosene so treated will vary greatly with the length of time that steam is passed through the kerosene. As an extreme instance, kerosene treated in this way for two days, when dried and distilled, gave with (approximately) 100 per cent. alcohol a C. T. S. = 12°, while the portion of

[1] See L. W. Andrews: J. Am. Chem. Soc., **30**, 353.

the oil which was volatile with water vapor, when dried, showed no cloudiness when mixed with an equal volume of 100 per cent. alcohol at a temperature of —8°. It is evident that the low boiling constituents of kerosene give with alcohol a much lower C. T. S. than the high boiling constituents and consequently variations in composition of kerosene will give corresponding variations of critical solution temperature. To use this method as a criterion of dehydration of alcohol would be hardly safe until one had set a standard for his particular sample of kerosene. We have relied entirely on the specific gravity method, and have made comparison tests by the kerosene method.

The pycnometer[1] used for the determination of specific gravity was of the Ostwald-Sprengel type and had a capacity of approximately 50 cc. It was provided with close-fitting, ground glass caps to prevent evaporation during weighing. This pycnometer was carefully calibrated several times and its capacity was known with a probable error of 0.0002 cc. It seems that little is to be gained by the use of a pycnometer larger than this unless one has a balance which is exceptionally sensitive under a heavy load. After bringing the pycnometer and its contents to the temperature of the bath, it was adjusted, wiped dry and allowed to stand some time in the balance case, when its weight was taken. In all our later work a duplicate pycnometer filled with water, whose caps were sealed on permanently with Khotinski wax, was carried through all these operations simultaneously and used as a *tare* in weighing. In this way errors due to deposition of moisture on the glass from the air were obviated. It is still better to avoid the use of caps on the tare by fusing the ends of the capillary tubes.

A number of samples of alcohol were dehydrated as above and their specific gravities were determined. The following values have been obtained within the last few months. In each case the alcohol was treated with silver nitrate and with calcium oxide twice besides the further treatment with calcium turnings and calcium oxide:

[1] The details of measurements with these and other types of pycnometers will be given in a monograph on alcohol.

Sample (1)	Treated with four portions of metallic calcium, sp. gr. =	0.785072
Sample (2)	Treated with calcium three times, sp. gr. =	0.785093
Sample (3)	Dried with calcium three times, sp. gr. =	0.785088
Sample (4)	Dried with calcium three times, sp. gr. =	0.785088
Sample (5)	Dried with calcium three times, sp. gr. =	0.785088
Sample (6)	Dried with calcium three times, sp. gr. =	0.785088
Sample (7)	Dried with calcium four times (middle portion of distillate), sp. gr. =	0.785069
Sample (8)	Dried with calcium six times (middle portion of distillate), *lowest sp. gr.* =	0.785058

It seems that under ordinary conditions anhydrous alcohol, obtained by the action of quicklime and calcium turnings on the commercial article, has a specific gravity of about 0.785085. By very complete dehydration and by fractional distillation somewhat lower figures may be obtained.

From this work it seems that the most probable value[1] for the specific gravity of alcohol is 0.78506 $\frac{25°}{4°}$. It should be stated that the specific gravity of water at 25° used for the above calculations was 0.997077, the value obtained by Chappuis,[2] and that the temperatures are on the hydrogen scale. Work on the physical constants of alcohol will be continued in this laboratory.

Purification of Alkyl Halides

Ethyl Iodide.—For the preparation of pure ethyl iodide, the best obtainable iodine was added to red phosphorus in 100 per cent. alcohol, and the resulting compound was washed well

[1] This value 0.78506 is identical with the one obtained by McKelvey and Osborne, of the National Bureau of Standards, in their very fine investigation on the physical properties of ethyl alcohol. See Circular No. 19 of the Bureau of Standards: Standard Density and Volumetric Tables.

[2] Thiesen: Wiss. Abh. Phys.-Techn. Reichsanst., **3**, 68 (1900). Chappuis: Bur. Int. d. Poids Mesures, Trav. Mém., **13** (1907).

with dilute alkalies and water. After drying it for a few minutes with calcium chloride, the dehydration was completed with a small quantity of resublimed phosphorus pentoxide. The alkyl halide was distilled from this through a dry condenser and again allowed to stand over phosphorus pentoxide. The dried liquid was subsequently redistilled several times in dried apparatus and thus obtained in good condition. The effect of light on the decomposition of these compounds being very marked, containing vessels of brown glass were used. By the addition of a few drops of mercury ethyl iodide may be kept entirely colorless. That there is no appreciable interaction between the two was shown by boiling ethyl iodide, under a return condenser, for three days with one-fifth its volume of mercury. Even with this vigorous treatment the action is slight, for it was found that only a little mercurous iodide was formed. On distilling the alkyl halide, a trace of mercury was found in the distillate. It is probable that at the boiling temperature a little mercury ethyl is formed, but, at ordinary temperatures, the quantity is not appreciable.

The boiling point of ethyl iodide[1] prepared as above was found to be 72°.14–72°.17 under 760 mm.

Methyl Iodide.—The methyl alcohol used in the preparation of methyl iodide contained about 0.1 per cent. water. Only the best iodine was used. Phosphorus pentoxide was used as above to remove the last traces of water and alcohol. After drying and redistilling, the methyl iodide was kept in dark bottles over a little mercury.

Since very discordant values are given by different authorities[2] for the boiling point and specific gravity of methyl iodide, careful determinations of both values were made. The thermometer used for the boiling-point determination was graduated in tenths of a degree. This thermometer was subsequently checked against a standard platinum resistance thermometer. The following values[3] were obtained:

[1] Mr. Meserve obtained 72°.20, and Mr. Shrader 72°.19, as the boiling point of ethyl iodide under 760 mm. at about 22°.

[2] Dobriner: Ann. Chem. (Liebig), **243**, 23. Perkin: J. prakt. Chem., [2] **31**, 500.

[3] Miss Brown obtained 42°.35, 42°.35, 42°.35–38, and 42°.31–36, as the boiling point of methyl iodide under 760 mm. at about 22°.

Sample I. Dried with phosphorus pentoxide and redistilled four times. B. p. = 42°.32—42°.34 under 759.35 mm. pressure

Sample II. Dried as above and redistilled twice. B. p. = 42°.25—42°.31 under 757.65 mm. pressure

The specific gravity of Sample (II) was found to be 2.2619 $\frac{25°}{4°}$.

Analysis:

0.7978 gram methyl iodide gave 1.3200 gram silver iodide.

	Gram found	Gram calculated
I	0.7135	0.7133

A number of analyses have shown that these alkyl halides can easily be prepared in a state of great purity, the foreign substances amounting to perhaps 0.01 to 0.05 per cent. The details will be given by Miss Brown and Messrs. Shrader and Meserve.

Phenol

The phenol used was Kahlbaum's best. It was twice redistilled and boiled from 180°.1 to 180°.2, uncorrected. After distillation it was pulverized and dried in vacuum desiccators over concentrated sulphuric acid for several weeks. After this treatment, it is improbable that more than traces of water were present. In making up solutions with phenol, care was taken not to expose it to the air more than was necessary, since it is quite hygroscopic and we desired to exclude all water from the reagents. A small box containing the balance, desiccator, flasks, etc., and fitted with a glass window, arm holes and rubber gloves, and also containing a drying agent, such as calcium chloride, through which the enclosed air is circulated by means of a fan, is quite necessary in transferring hygroscopic substances from the desiccator to the weighing tubes and volumetric apparatus. The temperature can also be regulated very easily. The apparatus will be described in detail in another article by Mr. Meserve.

Standard Acids and Alkalies

Hydrochloric acid was used for all titrations. It was standardized in several ways, all of which agreed satisfactorily.

The method of Acree and Brunel[1] is convenient and gives very satisfactory results. Dry, gaseous hydrochloric acid was passed into a flask containing a weighed quantity of water, precautions being taken to prevent loss of water vapor. The amount of acid absorbed was determined directly by weight and the solution thus obtained used as a standard in making up a large quantity of normal acid. In our most accurate work *weighed portions* were analyzed to within 0.01–0.02 per cent. and the correct volume determined by accurate measurements of the specific gravity.

Standard hydrochloric acid was also prepared by Hulett's method[2] and the results obtained were quite satisfactory. The acids obtained by these two methods were found to check one another within 0.1 per cent. Two gravimetric analyses of hydrochloric acid by Hulett's method were made, one giving 99.97 per cent. of the calculated weight of silver chloride and the other 100.07 per cent.

Standard sodium hydroxide was made from the purest metallic sodium by the use of sodium amalgam, and also by dropping small pieces of the sodium on ice water. It was thought that this gave a somewhat sharper titration with methyl orange than was given by alkalies containing carbonate. The alkali was standardized by titrating it against standard hydrochloric acid and also by evaporating a known volume with an excess of pure hydrochloric acid and weighing the residue of sodium chloride after ignition. Methyl orange was invariably used in all titrations.

Temperature Regulation

Constant temperatures were maintained by the use of two baths, the one for work at 25° having a capacity of about 450 liters, and the other for work at 35° having a capacity of 40 liters. Both were provided with efficient stirrers and there was no difficulty in keeping their temperatures permanently constant to within 0°.01, which was entirely satisfactory for reaction and conductivity work.

In making specific gravity determinations, however,

[1] This Journal, **38**, 117.

[2] Hulett and Bonner: J. Am. Chem. Soc., **31**, 390.

it was necessary to read temperatures somewhat closer than 0°.01. A Beckmann thermometer was therefore compared carefully with the standard and kept in the bath constantly for use in this work. In the pycnometric determinations of alcohol the temperature was read to within several thousandths of a degree and was probably correct to within 0°.004.

The standard thermometers used in this work have been calibrated to about 0°.002 at the National Bureau of Standards, or at the Bureau de Poids et Mesures at Sèvres, and have been checked by Dr. B. B. Turner in this laboratory against a standard platinum resistance thermometer of the Dickinson-Mueller type[1] as used in the United States Bureau of Standards, and somewhat modified by Dr. Turner and Acree. Our temperature standard is accurate to about 0°.002, which is much closer than we can rely upon any ordinary mercury thermometer. We shall describe later a special cathetometer and telescope, and the auxiliary apparatus, with which we can easily read primary standard thermometers to 0°.001 and good burettes to 0.001 cc.

Conductivity Measurements

The cells were of several types which we have designed in this laboratory and which will be described in another paper.[2] They seem to have an advantage over the older types in that they are far more constant and less subject to abrupt changes under careless handling.

The bridge wire, resistance box, etc., were carefully calibrated. Three readings of each resistance were taken at different points on the bridge wire and the results averaged, the mean values for the ionization μ_v/μ_∞ being given in Table XII. All conductivities are expressed in reciprocal ohms. The values used for μ_∞ were obtained by the direct measurement of the resistance of the N/2048, N/8096 and N/16182 solutions, which are practically completely ionized.

We have suspected for some time[3] that the differences in

[1] Bull. U. S. Bur. Standards., Vol. **3**, No. 4.

[2] Robertson and Acree: Address before the Int. Cong. Applied Chem., New York, September, 1912.

[3] Shadinger and Acree: THIS JOURNAL, **39**, 231; **44**, —, and later papers.

the viscosity of the different solutions will be found to have an influence on the velocity of movement of the different substances in solution and hence alter the reaction velocities in certain cases, and change the apparent per cent. of ionization of the various salts in the solution. If the ions of sodium ethylate move more slowly in the more viscous normal solutions than they do in the 0.1 N solutions, the conductivity measurements will not give us a true measure of the per cent. of ionization in the two cases. We should be compelled, therefore, to make a correction for the viscosity of the more concentrated solutions. No method is known at present, however, for doing this with certainty. One of us wrote of this problem to Professor A. A. Noyes, who at once kindly sent us two pages of a manuscript which he has since published.[1] Noyes' method is to multiply the apparent per cent. of ionization of the salt in a given solution by the ratio of the viscosity of this solution to that of the pure solvent. We have made measurements of the viscosities of various solutions of sodium ethylate, sodium phenolate, sodium iodide, and various mixtures of these, in absolute ethyl alcohol at 25° and 35°. The relation of the viscosities and conductivities of N, 0.5 N, and 0.25 N solutions of sodium phenolate and sodium ethylate, for example, are such that if we were to apply Noyes' method we should arrive at the conclusion that the per cent. of ionization is the same for the N, 0.5 N and 0.25 N solutions. Such a conclusion is, however, not in harmony with all the known facts of physical chemistry and certainly not borne out by our experimental results. We have thought of using some formula such as the expression $\alpha\sqrt{\frac{V_N}{V_o}}$ in which V_o and V_N are the viscosities of the pure solvent and of the solution studied. Until further work can be done by the use of *other methods* to give us a direct measure of the real ionic velocities we do not see any clear way to solve this problem. We are at present trying to measure the conductivities, the viscosities by Bingham's methods and the migration velocities and solvation by Washburn's methods in order to learn the true per cent. of ionization of our com-

[1] Noyes and Lombard: J. Am. Chem. Soc., **33**, 1424. Washburn: *Ibid.*, **33**, 1464.

pounds. We have tried to apply Noyes' correction, as well as our own, in determining whether the formula $K_N = K_i\alpha + K_N \frac{(\alpha)^2}{V}$ gives us constants for K_i and K_m when such correction is made (see page 480). The results have not been at all satisfactory. The best plan is to work with solutions which are so dilute that the viscosities are all practically the same as that of the pure solvent. It can be seen how great the difficulty is in making such a correction when it is realized that the viscosity of a N solution of sodium phenolate or sodium ethylate is nearly three times as large as that of the pure ethyl alcohol, and that the viscosity of our reaction mixtures is constantly changing. We have therefore extended our studies to regions as dilute as can possibly be measured with reasonable accuracy. It is a peculiar fact that our constants for K_i and K_m are practically the same for N solutions as for the dilute solutions, and we may find on further work that the "viscosity effects" influence the reaction velocities and the conductivities in such a way as to annul the errors discussed above. This field is a bright one for investigation. It is very fortunate for others who work with aqueous solutions that the viscosity of their most concentrated solutions is not greatly different from that of water; the errors cannot be very great in any case. We are measuring the viscosities of all of our solutions before and after the reactions are complete, and even during the reactions, to collect data which may shed light on this problem. We have also measured the change in volume in a number of cases, and have attempted to use the dilatometer in some cases to follow the velocity of the reaction. If the solution changes in volume there will be a corresponding change in the concentrations, for which we must make corrections. Certain energy changes will also be involved in the change of volume and these may be of great interest in the future. As we have pointed out before, chemists should consider in these studies every possible chemical and physical factor.

Measurements and Calculations of Reaction Velocities

The reactions were interrupted at the end of the desired

time-period by removing the small flask from the bath and pouring its contents into 200 cc. of cold distilled water, after which the titration with standard 0.2 N or 0.1 N hydrochloric acid was immediately made, and the amount of unchanged sodium phenolate thus determined. It was found by experiment that the above procedure involved no appreciable error, the progress of the reaction being practically reduced to zero by dilution with the large volume of cold water.

In the tables which follow, the constants have been calculated from the equations:

(1) $K_N/V = K_V = \frac{1}{t} \cdot \frac{x}{A - x}$ (for equivalent masses)

and

(2) $K_N/V = K_V = \frac{B}{t(B - A)} \log n \frac{B(A - x)}{A(B - x)}$ (for unequal masses)[1]

In this way both sets of velocity constants are referred to the same basis and become comparable.

The values given for A generally represent the actual volumes in cc. of the sodium phenolate solutions used. Under x is given the number of cc. of standard acid required for each titration, *referred to the same normality as the sodium phenolate solution used in that particular series of reactions.* These values of x therefore actually represent the volumes of A that have disappeared at the end of each time-period. K_N represents the velocity constant for each series when referred to the normal basis. It is obtained by multiplying the constant K_V by the dilution, V, in liters, of the sodium phenolate after mixture with the alkyl halide solution.

Summary

Tables I to XI and XIII and XIV illustrate the decrease in velocity of the reaction as increasing excesses of phenol are added. The general relations are shown in Table XI.

In Table XII we give the approximate ionization of sodium phenolate at 25° and 35° in solutions varying from N/1 to N/32. These have not yet been corrected for the influence of viscosity and solvation.

[1] Hecht, Conrad and Brückner: Z. physik. Chem., 8, 455.

Tables XIII to XXIV show the velocities of the reactions of sodium phenolate and methyl iodide at 25° in solutions varying from N/1 to N/32. Table XXV gives the average values for K_N, Table XXVI gives the values for K_i and K_m, and Table XXVII gives the values for "K_N found," "K_N calculated," and the experimental errors.

Tables XXVIII to XXXVIII give the velocity of transformation of sodium phenolate and methyl iodide at 35° in solutions varying from N/2 to N/40. Table XXXIX gives the average values for K_N, Table XL gives the values for K_i and K_m and Table XLI gives the values of "K_N found," "K_N calculated" and the experimental errors.

Tables XLII to LI give the reaction velocities for sodium phenolate and ethyl iodide at 25° in solutions varying from N/1 to N/16. Table LII gives the average values for K_N, Table LIII gives the values for K_i and K_m, and Table LIV gives the values "K_N found," "K_N calculated," and the experimental errors.

Tables LV to LXII give the reaction velocities for sodium phenolate and ethyl iodide at 35° in concentrations varying from N/2 to N/16. Table LXIII gives the average values of K_N, Table LXIV gives the values of K_i and K_m and Table LXV gives the values for "K_N found," "K_N calculated," and the experimental errors.

Table LXVI gives a résumé of all the values for K_i and K_m.

THE EFFECT OF AN EXCESS OF PHENOL ON THE REACTION VELOCITY AT 25°

Table I—0.5 N Sodium Phenolate and 0.25 N Methyl Iodide (no Excess Phenol) at 25°

$A = 10.02$

t	x	K_V
30	1.28	0.00488
40	1.62	0.00482
50	1.90	0.00468
60	2.16	0.00458
80	2.66	0.00452
100	3.09	0.00446

Average $K_V = 0.00466$

Table II—0.5 N Sodium Phenolate and 0.5 N Methyl Iodide (no Excess Phenol) at 25°

$A = 10.00$

t	x	K_V
40	1.62	0.00483
50	1.95	0.00484
60	2.17	0.00462
80	2.70	0.00462
100	3.14	0.00458
140	3.86	0.00449

Average $K_V = 0.00466$

For Reactions with 1 per cent. Excess Phenol, see Tables XII and XIII.

Table III—0.5 N Sodium Phenolate and 0.5 N Methyl Iodide (2 per cent. Excess Phenol) at 25°

A = 10.00

t	x	K_V
30	1.22	0.00463
40	1.54	0.00455
50	1.88	0.00463
65	2.31	0.00462
75	2.54	0.00454
90	2.84	0.00441

Average K_V = 0.00456

Table IV—0.5 N Sodium Phenolate and 0.5 N Methyl Iodide (2 per cent. Excess Phenol) at 25°

A = 10.00

t	x	K_V
30	1.20	0.00454
40	1.53	0.00451
50	1.86	0.00457
60	2.14	0.00454
70	2.44	0.00460
100	3.09	0.00447

Average K_V = 0.00454

Table V—0.5 N Sodium Phenolate and 0.5 N Methyl Iodide (5 per cent. Excess Phenol) at 25°

A = 10.04

t	x	K_V
30	1.15	0.00431
40	1.47	0.00428
50	1.77	0.00428
60	2.06	0.00430
70	2.32	0.00429
90	2.99	0.00428

Average K_V = 0.00429

Table VI—0.5 N Sodium Phenolate and 0.5 N Methyl Iodide (5 per cent. Excess Phenol) at 25°

A = 10.01

t	x	K_V
30	1.16	0.00436
40	1.48	0.00434
50	1.79	0.00435
60	2.06	0.00432
100	3.04	0.00436

Average K_V = 0.00435

Table VII—0.5 N Sodium Phenolate and 0.5 N Methyl Iodide (10 per cent. Excess Phenol) at 25°

A = 10.04

t	x	K_V
20	0.76	0.00409
30	1.12	0.00418
40	1.42	0.00412
50	1.73	0.00416
60	1.98	0.00409
80	2.48	0.00410

Average K_V = 0.00412

Table VIII—0.5 N Sodium Phenolate and 0.5 N Methyl Iodide (10 per cent. Excess Phenol) at 25°

A = 10.05

t	x	K_V
20	0.754	0.00406
30	1.106	0.00412
40	1.44	0.00418
50	1.69	0.00404
60	1.97	0.00406

Average K_V = 0.00409

Table IX—0.5 N Sodium Phenolate and 0.5 N Methyl Iodide (20 per cent. Excess Phenol) at 25°

$A = 10.01$

t	x	K_V
20	0.71	0.00382
40	1.34	0.00386
50	1.65	0.00395
60	1.90	0.00390
90	2.62	0.00395
260	5.05	0.00391

Average $K_V = 0.00390$

Table X—0.5 N Sodium Phenolate and 0.5 N Methyl Iodide (30 per cent. Excess Phenol) at 24°.95

$A = 10.01$

t	x	K_V
30	0.99	0.00365
40	1.28	0.00367
50	1.57	0.00372
60	1.80	0.00365
80	2.27	0.00366
100	2.69	0.00367
123	3.10	0.00365

Average $K_V = 0.00367$

Table XI—Resume of the Reaction Velocities for 0.5 N Sodium Phenolate, 0.5 N Methyl Iodide and an Excess of Phenol at 25°

Excess of phenol in per cent.	K_V	K_V calculated
0	0.00466	0.00467
1	0.00462	0.00463
2	0.00455	0.00460
5	0.00432	0.00450
10	0.00410	0.00432
20	0.00390	0.00397
30	0.00367	0.00362

Table XII—The Ionization of Sodium Phenolate at 25° and 35°

Ionization at 25°

V	α	$1-\alpha$
1	0.122	0.878
2	0.189	0.811
4	0.258	0.742
8	0.335	0.665
16	0.419	0.581
32	0.509	0.491

Ionization at 35°

V	α	$1-\alpha$
2	0.185	0.815
4	0.247	0.753
8	0.319	0.681
16	0.399	0.601
32	0.486	0.514
40	0.516	0.484

REACTIONS BETWEEN SODIUM PHENOLATE AND METHYL IODIDE AT 25°

Table XIII—1 N Sodium Phenolate and 1 N Methyl Iodide at 25°

A = 10.00

t	x	K_V
20	1.33	0.00780
30	1.87	0.00766
40	2.35	0.00767
50	2.78	0.00770
60	3.14	0.00762
80	3.75	0.00750

Average K_V = 0.00766
K_N = 0.00766

Table XIV—1 N Sodium Phenolate and 1 N Methyl Iodide at 25°

A = 10.00

t	x	K_V
20	1.34	0.00773
30	1.87	0.00766
40	2.34	0.00764
50	2.74	0.00755
60	3.11	0.00752

Average K_V = 0.00762
K_N = 0.00762

Table XV—0.5 N Sodium Phenolate and 0.5 N Methyl Iodide at 25°

A = 10.00

t	x	K_V
30	1.24	0.00471
40	1.56	0.00462
51	1.91	0.00462
60	2.18	0.00464
70	2.45	0.00464
80	2.66	0.00452
100	3.14	0.00457

Average K_V = 0.00462
K_N = 0.00924

Table XVI—0.5 N Sodium Phenolate and 0.5 N Methyl Iodide at 25°

A = 9.98

t	x	K_V
21	0.91	0.00478
30	1.22	0.00464
40	1.56	0.00463
50	1.88	0.00465
60	2.16	0.00460
80	2.65	0.00452
120	3.52	0.00454

Average K_V = 0.00462
K_N = 0.00924

Table XVII—0.25 N Sodium Phenolate and 0.25 N Methyl Iodide at 25°

A = 10.00

t	x	K_V
30	0.736	0.00265
40	0.98	0.00271
50	1.18	0.00267
60	1.39	0.00269
70	1.56	0.00264
82	1.77	0.00262
150	2.80	0.00259

Average K_V = 0.00265
K_N = 0.01060

Table XVIII—0.25 N Sodium Phenolate and 0.25 N Methyl Iodide at 25°

A = 10.00

t	x	K_V
50	1.20	0.00273
60	1.41	0.00274
70	1.59	0.00270
90	1.92	0.00265
100	2.12	0.00269
110	2.29	0.00269

Average K_V = 0.00270
K_N = 0.01080

Table XIX—0.125 N Sodium Phenolate and 0.25 N Methyl Iodide at 25°

$A = 10.00$ $B = 20.00$

t	x	K_V
40	1.18	0.00162
54	1.52	0.00159
65	1.78	0.00158
75	1.99	0.00156
85	2.22	0.00157
100	2.52	0.00156

Average $K_V = 0.00158$
$K_N = 0.01264$

Table XX—0.125 N Sodium Phenolate and 0.25 N Methyl Iodide at 25°

$A = 10.00$ $B = 20.00$

t	x	K_V
40	1.20	0.00165
50	1.44	0.00161
60	1.66	0.00158
70	1.91	0.00159
80	2.14	0.00160
100	2.56	0.00158

Average $K_V = 0.00160$
$K_N = 0.01280$

Table XXI—0.0625 N Sodium Phenolate and 0.25 N Methyl Iodide at 25°

$A = 10.00$ $B = 40.00$

t	x	K_V
40	1.32	0.000900
50	1.66	0.000928
60	1.90	0.000900
70	2.20	0.000914
80	2.42	0.000894

Average $K_V = 0.000907$
$K_N = 0.01451$

Table XXII—0.0625 N Sodium Phenolate and 0.25 N Methyl Iodide at 25°

$A = 20.00$ $B = 80.00$

t	x	K_V
50	3.27	0.000912
60	3.84	0.000911
70	4.34	0.000909
80	4.87	0.000901
90	5.33	0.000893
100	5.79	0.000889

Average $K_V = 0.000902$
$K_N = 0.01443$

Table XXIII—0.03125 N Sodium Phenolate and 0.25 N Methyl Iodide at 25°

$A = 20.00$ $B = 160.00$

t	x	K_V
70	5.06	0.000529
80	5.63	0.000525
90	6.24	0.000529
100	6.69	0.000520
110	7.20	0.000520
120	7.67	0.000517

Average $K_V = 0.000523$
$K_N = 0.01674$

Table XXIV—0.03125 N Sodium Phenolate and 0.25 N Methyl Iodide at 25°

$A = 20.00$ $B = 160.00$

t	x	K_V
60	4.51	0.000539
70	5.03	0.000525
80	5.60	0.000523
90	6.16	0.000522
100	6.69	0.000520

Average $K_V = 0.000526$
$K_N = 0.01683$

Table XXV—K_N Found for Sodium Phenolate and Methyl Iodide at 25°

Conc. $NaOC_6H_5$ / V	K_N	Average K_N
1	0.00766	
	0.00762	0.00764
2	0.00924	
	0.00924	0.00924
4	0.01060	
	0.01080	0.01070
8	0.01264	
	0.01280	0.01272
16	0.01451	
	0.01443	0.01447
32	0.01674	
	0.01683	0.01678

Table XXVI—K_i and K_m Found for Sodium Phenolate and Methyl Iodide at 25°

	K_i	K_m
$V = 1 : V = 2$	0.0286	0.00473
$V = 1 : V = 4$	0.0274†	0.00489†
$V = 1 : V = 8$	0.0286*	0.00473*
$V = 1 : V = 16$	0.0278*	0.00483*
$V = 1 : V = 32$	0.0283*	0.00476*
$V = 2 : V = 4$	0.0264	0.00524
$V = 2 : V = 8$	0.0286†	0.00473†
$V = 2 : V = 16$	0.0276*	0.00494*
$V = 2 : V = 32$	0.0283*	0.00478*
$V = 4 : V = 8$	0.0300	0.00393
$V = 4 : V = 16$	0.0281†	0.00466†
$V = 4 : V = 32$	0.0286*	0.00445*
$V = 8 : V = 16$	0.0266	0.00574
$V = 8 : V = 32$	0.0282†	0.00490†
$V = 16 : V = 32$	0.0294	0.00372
Average	0.0282	0.00474
Average[1]	0.02815	0.00477
Average[2]	0.0282	0.00475

[1] The average of all the values with daggers and asterisks.
[2] The average of all the values with asterisks.

Table XXVII—K_N Calculated and Found for Sodium Phenolate and Methyl Iodide at 25°

V	α	$1-\alpha$	K_N found	K_N calculated	Error in per cent.
1	0.122	0.878	0.00764	0.00760	+0.5
2	0.189	0.811	0.00924	0.00917	+0.8
4	0.258	0.742	0.01070	0.01079	—0.8
8	0.335	0.665	0.01272	0.01260	+1.0
16	0.419	0.581	0.01447	0.01457	—0.7
32	0.509	0.491	0.01678	0.01668	+0.6

REACTIONS BETWEEN SODIUM PHENOLATE AND METHYL IODIDE AT 35°

Table XXVIII—0.5 N Sodium Phenolate and 0.5 N Methyl Iodide at 35°

$A = 9.98$

t	x	K_V
20	2.18	0.01397
30	2.93	0.01385
40	3.55	0.01381
50	4.08	0.01383
60	4.50	0.01368

Average $K_V = 0.01383$

$K_N = 0.02766$

Table XXIX—0.5 N Sodium Phenolate and 0.5 N Methyl Iodide at 35°

$A = 10.00$

t	x	K_V
30	2.98	0.01412
40	3.60	0.01406
50	4.13	0.01407
60	4.53	0.01381
72	4.96	0.01367
85	5.42	0.01392

Average $K_V = 0.01394$

$K_N = 0.02788$

Table XXX—0.25 N Sodium Phenolate and 0.25 N Methyl Iodide at 35°

$A = 9.98$

t	x	K_V
40	2.44	0.00808
50	2.86	0.00808
60	3.21	0.00791
70	3.59	0.00802
100	3.89	0.00798
	4.39	0.00785

Average $K_V = 0.00798$

$K_N = 0.03192$

Table XXXI—0.25 N Sodium Phenolate and 0.25 N Methyl Iodide at 35°

$A = 10.00$

t	x	K_V
30	1.94	0.00802
40	2.43	0.00802
50	2.84	0.00793
60	3.23	0.00795
70	3.58	0.00795
80	3.89	0.00793

Average $K_V = 0.00797$

$K_N = 0.03188$

Table XXXII—0.125 N Sodium Phenolate and 0.125 N Methyl Iodide at 35°

$A = 10.00$

t	x	K_V
50	1.98	0.00493
60	2.24	0.00481
70	2.52	0.00481
80	2.77	0.00482
90	2.98	0.00472

Average $K_V = 0.00482$

$K_N = 0.03856$

Table XXXIII—0.125 N Sodium Phenolate and 0.25 N Methyl Iodide at 35°

$A = 10.00$ $B = 20.00$

t	x	K_V
20	1.66	0.00474
30	2.42	0.00492
40	3.02	0.00490
50	3.52	0.00481
60	3.95	0.00472
70	4.39	0.00472

Average $K_V = 0.00480$

$K_N = 0.03840$

Table XXXIV—0.0625 N Sodium Phenolate and 0.125 N Methyl Iodide at 35°

$A = 20.00$ $B = 40.00$

t	x	K_V
75	6.34	0.00278
80	6.72	0.00282
90	7.30	0.00281
100	7.84	0.00279
110	8.24	0.00281

Average $K_V = 0.00280$

$K_N = 0.04480$

Table XXXV—0.0625 N Sodium Phenolate and 0.25 N Methyl Iodide at 35°

$A = 10.00$ $B = 39.904$

t	x	K_V
45	3.815	0.00281
55	4.373	0.00279
65	4.821	0.00272
75	5.331	0.00276
85	5.674	0.00269
95	6.010	0.00266

Average $K_V = 0.00274$

$K_N = 0.0444$

Table XXXVI — 0.03125 N Sodium Phenolate and 0.25 N Methyl Iodide at 35°

$A = 20.00$ $B = 160.00$

t	x	K_V
60	10.37	0.00158
70	11.36	0.00156
80	12.35	0.00157
90	13.32	0.00160

Average $K_V = 0.00158$

$K_N = 0.05056$

Table XXXVII—0.03125 N Sodium Phenolate and 0.125 N Methyl Iodide at 35°

$A = 20.00$ $B = 80.00$

t	x	K_V
60	6.37	0.00167
70	7.04	0.00163
80	7.78	0.00162
100	8.96	0.00159
110	9.60	0.00159

Average $K_V = 0.00162$

$K_N = 0.0518$

Table XXXVIII — 0.025 N Sodium Phenolate and 0.25 N Methyl Iodide at 35°

$A = 40.00$ $B = 400.00$

t	x	K_V
45	17.96	0.00136
75	24.60	0.00132
90	27.50	0.00134
110	29.80	0.00130

Average $K_V = 0.00133$
$K_N = 0.0532$

Table XXXIX—K_N Found for Sodium Phenolate and Methyl Iodide at 35°

Conc. $\frac{NaOC_6H_5}{V}$	K_N	Average K_N
2	0.02766 0.02788	0.02777
4	0.03192 0.03188	0.03190
8	0.03856 0.03840	0.03843
16	0.04480 0.04440	0.04460
32	0.05056 0.05180	0.05120
40	0.05320	0.05320

Table XL—K_i and K_m Found for Sodium Phenolate and Methyl Iodide at 35°

	K_i	K_m
$V = 2 : V = 4$	0.082	0.0155
$V = 2 : V = 8$	0.093	0.0130
$V = 2 : V = 16$	0.092	0.0133
$V = 2 : V = 32$	0.093	0.0134
$V = 4 : V = 8$	0.101	0.0093
$V = 4 : V = 16$	0.095	0.0113
$V = 4 : V = 32$	0.092	0.0120
$V = 8 : V = 16$	0.090	0.0141
$V = 8 : V = 32$	0.090	0.0143
$V = 16 : V = 32$	0.090	0.0143
$V = 2 : V = 40$	0.090	0.0136
$V = 4 : V = 40$	0.091	0.0123
$V = 8 : V = 40$	0.089	0.0144
Average	0.091	0.0131

Table XLI—K_N Calculated and Found for Sodium Phenolate and Methyl Iodide at 35°

V	K_N Found	K_N Calculated	Error in per cent.
2	0.0278	0.0275	+1.1
4	0.0319	0.0323	—1.2
8	0.0385	0.0379	+1.6
16	0.0448	0.0442	+0.9
32	0.0506	0.0509	+0.6
40	0.0532	0.0533	—0.2

REACTIONS BETWEEN SODIUM PHENOLATE AND ETHYL IODIDE AT 25°

Table XLII—1 N Sodium Phenolate and 1 N Ethyl Iodide at 25°

$A = 9.96$

t	x	K_V
50	0.712	0.00154
60	0.86	0.00157
80	1.09	0.00153
95	1.285	0.00158
120	1.54	0.00153

Average $K_V = 0.00155$
$K_N = 0.00155$

Table XLIII—1 N Sodium Phenolate and 1 N Ethyl Iodide at 25°

$A = 10.00$

t	x	K_V
30	0.455	0.001554
43	0.626	0.001552
57	0.830	0.001584
68	0.954	0.001551
79	1.090	0.001548
90	1.226	0.001553

Average $K_V = 0.001557$
$K_N = 0.001557$

Table XLIV—0.5 N Sodium Phenolate and 1 N Ethyl Iodide at 25°

$A = 10.00$ $B = 20.00$

t	x	K_V
30	0.54	0.000937
50	0.86	0.000919
60	1.01	0.000912
70	1.19	0.000932
80	1.34	0.000932

Average $K_V = 0.000926$
$K_N = 0.001852$

Table XLV—0.5 N Sodium Phenolate and 0.5 N Ethyl Iodide at 25°

$A = 10.00$

t	x	K_V
60	0.530	0.000930
70	0.610	0.000928
80	0.710	0.000955
90	0.770	0.000927
100	0.836	0.000912
110	0.908	0.000908

Average $K_V = 0.000927$
$K_N = 0.001854$

Table XLVI—0.25 N Sodium Phenolate and 1 N Ethyl Iodide at 25°

$A = 9.98$ $B = 39.92$

t	x	K_V
30	0.65	0.000566
45	0.96	0.000568
60	1.186	0.000534
70	1.33	0.000518
90	1.70	0.000529
115	2.18	0.000550

Average $K_V = 0.000544$
$K_N = 0.002176$

Table XLVII—0.25 N Sodium Phenolate and 0.5 N Ethyl Iodide at 25°

$A = 10.00$ $B = 20.00$

t	x	K_V
70	0.71	0.000527
80	0.80	0.000532
90	0.91	0.000543
100	0.99	0.000535
110	1.11	0.000550
120	1.20	0.000550

Average $K_V = 0.000546$
$K_N = 0.002184$

Table XLVIII—0.125 N Sodium Phenolate and 0.5 N Ethyl Iodide at 25°

$A = 10.00$ $B = 40.00$

t	x	K_V
60	0.71	(0.000309)
70	0.85	0.000320
80	0.95	0.000316
90	1.06	0.000316
100	1.18	0.000318
110	1.27	0.000313

$K_V = 0.0003166$
$K_N = 0.002533$

Table XLIX—0.125 N Sodium Phenolate and 0.5 N Ethyl Iodide at 25°

$A = 20.00$ $B = 80.00$

t	x	K_V
60	1.44	0.000322
70	1.68	0.000317
80	1.91	0.000317
90	2.14	0.000319
100	2.35	0.000317
110	2.54	0.000315

Average $K_V = 0.000318$
$K_N = 0.002544$

Table L—0.0625 N Sodium Phenolate and 0.5 N Ethyl Iodide at 25°

$A = 10.00$ $B = 80.00$

t	x	K_V
61	0.84	0.000181
75	1.04	0.000184
90	1.25	0.000187
105	1.42	0.000184
120	1.58	0.000180
140	1.80	0.000179

Average $K_V = 0.000182$
$K_N = 0.00292$

Table LI—0.0625 N Sodium Phenolate and 0.5 N Ethyl Iodide at 25°

$A = 20.00$ $B = 160.00$

t	x	K_V
60	1.68	0.000184
70	1.91	0.000181
80	2.15	0.000180
90	2.40	0.000179
100	2.64	0.000178

Average $K_V = 0.0001804$
$K_N = 0.00289$

Table LII—K_N Found for Sodium Phenolate and Ethyl Iodide at 25°

V	K_N	Average K_N
1	0.00155 0.00156	0.00155
2	0.00185 0.00185	0.00185
4	0.00216 0.00218	0.00217
8	0.00254 0.00254	0.00254
16	0.00289 0.00292	0.00290

Table LIII—K_i and K_m Found for Sodium Phenolate and Ethyl Iodide at 25°

	K_i	K_m
$V = 1 : V = 2$	0.0055	0.00100
$V = 1 : V = 4$	0.0056	0.00099
$V = 1 : V = 8$	0.0056	0.00098
$V = 1 : V = 16$	0.0058	0.00099
$V = 2 : V = 4$	0.0056	0.00097
$V = 2 : V = 8$	0.0057	0.00096
$V = 2 : V = 16$	0.0056	0.00099
$V = 4 : V = 8$	0.0054	0.00093
$V = 4 : V = 16$	0.0055	0.00100
$V = 8 : V = 16$	0.0054	0.00110
Average	0.0056	0.00099

Table LIV—K_N Found and Calculated for Sodium Phenolate and Ethyl Iodide at 25°

V	K_N Found	K_N Calculated	Error in per cent.
1	0.00155	0.00155	0.00
2	0.00185	0.00186	—0.50
4	0.00217	0.00218	—0.50
8	0.00254	0.00253	+0.40
16	0.00290	0.00292	—0.60

REACTIONS BETWEEN SODIUM PHENOLATE AND ETHYL IODIDE AT 35°

Table LV — 0.5 N Sodium Phenolate and 0.5 N Ethyl Iodide at 35°

$A = 9.98$

t	x	K_V
40	1.09	0.00306
50	1.32	0.00305
60	1.53	0.00302
70	1.74	0.00302
80	1.98	0.00299

Average $K_V = 0.00303$
$K_N = 0.00606$

Table LVI—0.5 N Sodium Phenolate and 0.5 N Ethyl Iodide at 35°

$A = 9.97$

t	x	K_V
40	1.09	0.00307
50	1.30	0.00300
60	1.54	0.00304
70	1.73	0.00300
80	1.92	0.00298

Average $K_V = 0.00302$
$K_N = 0.00604$

Table LVII—0.25 N Sodium Phenolate and 0.25 N Ethyl Iodide at 35°

$A = 19.94$

t	x	KV
40	1.33	0.00178
50	1.60	0.00175
60	1.88	0.00174
70	2.17	0.00174
80	2.46	0.00176

Average $K_V = 0.00176$
$K_N = 0.00704$

Table LVIII—0.25 N Sodium Phenolate and 0.50 N Ethyl Iodide at 34°.9[1]

$A = 10.00$ $B = 19.96$

t	x	K_V
40	1.25	0.001728
50	1.54	0.001746
60	1.82	0.001762
70	2.08	0.001766
80	2.28	0.001725
90	2.48	0.001700

Average $K_V = 0.001738$
K_N (34°.9) $= 0.006952$
K_N (35°.0) $= 0.00701$

Table LIX—0.125 N Sodium Phenolate and 0.5 N Ethyl Iodide at 35°

$A = 20.00$ $B = 80.00$

t	x	K_V
40	2.92	0.001006
60	4.14	0.000993
80	5.26	0.000988
100	6.36	0.000999
120	7.28	0.000993
140	8.20	0.000999

Average $K_V = 0.000996$
$K_N = 0.00797$

Table LX—0.125 N Sodium Phenolate and 0.5 N Ethyl Iodide at 35°.1

$A = 10.00$ $B = 40.00$

t	x	K_V
50	1.82	0.001029
60	2.12	0.001021
75	2.56	0.001020
80	2.66	0.001002
90	3.00	0.001032

Average $K_V = 0.001021$
$K_N(35°.1) = 0.00817$
$K_N(35°) = 0.00807$

[1] In these experiments the temperature of the bath was 34°.9. We have therefore used the equation $K_T = K_{T_0} \times 10\,(0.0526\,T - 0.0526\,T_0)$ (Hecht and Conrad: Z. physik. Chem., **3**, 465) to correct for 35°.0.

Table LXI—0.0625 N Sodium Phenolate and 0.25 N Ethyl Iodide at 35°

$A = 20.00$ $B = 80.00$

t	x	K_V
40	1.78	0.000589
50	2.16	0.000579
60	2.58	0.000585
70	3.02	0.000587
80	3.31	0.000578

Average $K_V = 0.000584$
$K_N = 0.00934$

Table LXII—0.0625 N Sodium Phenolate and 0.25 N Ethyl Iodide at 35°.1

$A = 20.00$ $B = 80.00$

t	x	K_V
50	2.20	0.000592
60	2.58	0.000585
70	3.04	0.000600
80	3.39	0.000593
90	3.67	0.000577

Average $K_V = 0.000590$
$K_N(35°.1) = 0.00944$
$K_N(35°) = 0.00933$

Table LXIII—K_N Found for Sodium Phenolate and Ethyl Iodide at 35°

Conc. $NaOC_6H_5$ V	K_N	Average K_N
2	0.00604 0.00606	0.00605
4	0.00704 0.00701[1]	0.00702
8	0.00807[1] 0.00797	0.00802
16	0.00934 0.00933[1]	0.00933

Table LXIV—K_i and K_m Found for Sodium Phenolate and Ethyl Iodide at 35°

	K_i	K_m
$V = 2 : V = 4$	0.0188	0.00315
$V = 2 : V = 8$	0.0181	0.00333
$V = 2 : V = 16$	0.0185	0.00321
$V = 4 : V = 8$	0.0175	0.00359
$V = 4 : V = 16$	0.0185	0.00327
$V = 8 : V = 16$	0.0191	0.00280
Average	0.0184	0.00323

[1] These constants were calculated for 35° from the data obtained experimentally at 34°.9 and 35°.1.

Table LXV—K_N Calculated and Found for Sodium Phenolate and Ethyl Iodide at 35°

V	K_N Found	K_N Calculated	Error in per cent.
2	0.00605	0.00604	+0.2
4	0.00702	0.00698	+0.6
8	0.00802	0.00806	—0.5
16	0.00933	0.00928	+0.5

Table LXVI—Resume of All the Values for K_i and K_m

	K_i	K_m
Sodium phenolate and methyl iodide at 25°.	0.0282	0.00474
Sodium phenolate and methyl iodide at 35°	0.091	0.0131
Sodium phenolate and ethyl iodide at 25°	0.0056	0.00099
Sodium phenolate and ethyl iodide at 35°	0.0184	0.00323

CONCLUSIONS

1. In this article we have shown that the theory that only the ionized portions of electrolytes are chemically active is only partially correct, and that much of the earlier work on which this theory was based was interpreted unfortunately. We should therefore consider the possibility that both the ions and the nonionized forms of electrolytes may undergo transformation with comparable velocities, which may be influenced by so-called "salt effects" and other physical factors. With this theory in mind, the work presented here was undertaken.

2. A full description of the apparatus and quantitative methods is given in the experimental portion.

3. A list of tables is given in which we present the velocities of the reactions of sodium phenolate with methyl iodide and with ethyl iodide at 25° and 35° in absolute ethyl alcohol, the concentrations varying from N/1 to N/40.

4. The proper numerical data are substituted in a general formula, $K_N = K_i\alpha + K_m(1-\alpha)$, and the series of simultaneous equations so obtained are solved. Constant values are obtained for K_i and K_m, which represent the velocity of

transformation of unit concentrations of phenolate ions, nonionized sodium phenolate and alkyl halides. We have interpreted this fact as evidence that both the phenolate ions and the nonionized sodium phenolate react with the nonionized alkyl halides, although we wish to point out that there may be an "abnormal salt effect" not yet understood.

5. If this theory is correct, the same value should be obtained for K_i, the velocity of transformation of unit concentrations of the phenolate ions and a given alkyl halide, whether the source of the phenolate ions be the sodium, potassium, lithium or other salts. The work reported here and other studies by Mr. Shrader, which are touched on now and will be reported in detail later, are discussed on pages 483 and 484, and it is shown there that the same alkyl halide actually does give practically the same value for K_i for sodium, potassium and lithium phenolates.

6. We suspect that the values for K_i and K_m given here may involve an "abnormal salt effect," which we shall next try to determine by measuring the reaction velocities in solutions varying from N/1 to N/2048, if possible. A similar study has already been made by Dr. C. N. Myers, who has shown that *p*-bromobenzonitrile and sodium, potassium and lithium ethylates, in solutions varying from N/32 to N/2048, give the same value for K_i for the ethylate ion in these *ideal solutions*, but *apparently different uncorrected values* for K_i and K_m in the more concentrated solutions.

7. We are investigating these peculiarities, or abnormalities, of these concentrated solutions (absolute alcohol) as rapidly as possible by attempting to measure their physical properties, especially the fluidities of the solutions by Bingham's methods, the effect of added salts on the reaction velocities, and the probable extent of the solvation (alcoholation) of the reacting constituents by Washburn's methods. These *physical factors* and the *electronic phenomena* probably play a role having far greater significance than we can possibly understand with our present knowledge.

JOHNS HOPKINS UNIVERSITY
June 1, 1910

REVIEWS

TREATISE ON GENERAL AND INDUSTRIAL INORGANIC CHEMISTRY. By ETTORE MOLINARI, Professor of Industrial Chemistry to the Society for the Encouragement of Arts and Manufactures of Merceology at the Commercial University Luigi Bocconi at Milan. Third Revised and Amplified Italian Edition. Translated by ERNEST FEILMANN, B.Sc., PH.D., F. I. C. With 280 illustrations in the text and one chromolithographic plate and two phototype plates. Philadelphia: P. Blakiston's Son & Co. 1912. Pp. xvi + 704. Price, $6.00.

In the preface to the first edition of this book the author says: "General and inorganic chemistry should no longer be a simple and arid expression of fundamental laws and of the properties of innumerable known substances, but should possess a soul which brings it into contact with the vital activities around which it clings. In a course of general inorganic chemistry all the applications which have been made of the fundamental laws and of the properties of substances should be studied. The chemical text-books which have been used until now do not correspond sufficiently to these requirements, and it is only since a couple of years that attempts have been made to reform this state of affairs and to carry into practice the improvements which have been urgently demanded from several quarters.

"I am far from believing that this book may be considered as a treatise on chemical technology but it is my conviction that industrial chemistry must start from the foundations of general chemical culture embodied in this treatise, in order to enter into all the technical and economic conditions of manufacture of the more important compounds, and in order to place the young chemist in a position to assume the direction of and collaboration in our chemical industry with more success and utility."

Whatever views one may hold in regard to the value of instruction in chemical technology in the early stages of the student's course, all will agree that statements in regard to applications of substances and principles add to the interest of the treatment, and they are, therefore, desirable. It is in statements of this kind that the book before us differs most markedly from other text-books now in use.

In Part I those subjects which are generally treated of under the head of theoretical chemistry are taken up. Here will be found interesting, though brief, discussions of the fundamental laws and principles of chemistry: osmotic pressure; electrolytic dissociation; equilibrium in heterogeneous systems and the phase rule; radioactivity and the unity of matter.

The real value of the book depends upon the statements concerning industrial applications. No book known to the writer of this notice can at all compare with it in this respect, and every chemist will be interested in the statements bearing upon these subjects.

While turning the leaves I find on page 133 this, which may be well known to many, but is certainly not known to many others: "In the Russo-Japanese War (1904–05) the Russians found it convenient, in order to avoid the transport to and fro of heavy steel cylinders, of compressed hydrogen for their balloons on the field of battle, to produce hydrogen as required on the spot (in Manchuria) by the action of 30 per cent. caustic soda solution on aluminium scrap." * * * * "In the Boer War the British employed hydrogen compressed to 200 atmospheres in steel cylinders, and required fifty horses for the transport of all materials for a balloon of 400 cubic meters."

Under Sterilization of Water is found this statement: "Of all methods of sterilization proposed up to the present the safest and most economic is the treatment of the water with ozone. In 1891, Dr. Ohmüller first investigated the behavior of thevarious species of bacteria in the presence of slightly ozonized air and succeeded in showing that none of the pathogenic bacteria, especially when distributed in water, resisted the action of ozone, even when much diluted. The *Bacteria subtilis* (hay microbe) alone resists the action of ozone (and also a temperature of 110°), but it is a perfectly inoffensive organism, both for man and for animals.

"From that time the solution of the great problem of the sterilization of water only awaited the time when it would be possible to obtain ozone cheaply and in large quantity.

"To-day the solution of the problem is an accomplished fact and there are in Europe many important plants for the ozonization of water."

Twenty-six pages are given to the subject of sulphuric acid; ten and a half pages to the utilization of atmospheric nitrogen; eighteen pages to the element carbon in its different forms.

Another interesting illustration of the thoroughness of the author's method will be found under the head "Aluminium Silicate." The subjects treated of under this head are ceramic industry; porcelain; bricks and tiles; artificial bricks and stones; hydraulic mortar and cements; natural cements; Roman cements; natural and artificial Portland cements; manufacture of artificial cements; cement burning kilns; rotary kilns; cement testing; applications and statistics—twenty-five pages being taken for these subjects.

It is perhaps needless to add that iron in its various forms receives full treatment. The metallurgy of iron is discussed in twelve pages, and then follows a section on the micrography of iron and steel.

The latest statistics are given in an appendix and it is noted that in many cases these are brought down to the year 1911.

The book can be cordially recommended to all chemists.

I. R.

JAHRBUCH DER CHEMIE. Bericht über die wichtigsten Fortschritte der reinen und angewandten Chemie. Unter Mitwirkung von H. BECKURTS (Braunschweig), M. DELBRÜCK (Berlin), J. M. EDER (Wien), H. FREUNDLICH (Braunschweig), P. FRIEDLAENDER (Darmstadt), C. HAEUSSERMANN (Ludwigsburg), A. HERZFELD (Berlin), EDV. HJELT (Helsingfors), K. A. HOFMANN (Berlin), G. KEPPELER (Hannover), E. KNECHT (Manchester), J. LEWKOWITSCH (London), A. MORGEN (Hohenheim), B. NEUMANN (Darmstadt), M. NIERENSTEIN (Bristol), P. RONA (Berlin), herausgegeben von RICHARD MEYER (Braunschweig). XXI. Jahrgang. 1911. Braunschweig: Druck und Verlag von Friedrich. Vieweg und Sohn. 1912.

The only change in the personnel of the editorial board of this Annual is the substitution of Professor Herbert Freundlich, of Braunschweig, for Dr. Sackur for the report on Physical Chemistry. The high standard of the publication is maintained, and as has been stated in previous notices it is indispensable for working chemists. It has the advantage of being brief and yet not so brief as to be indigestible. It is made up of the reports enumerated below:

I. Physical Chemistry. By Herbert Freundlich.
II. Inorganic Chemistry. By K. E. Hofmann.
III. Organic Chemistry. By Edv. Hjelt.
IV. Physiological Chemistry. By Peter Rona.
V. Pharmaceutical Chemistry. By Heinr. Beckurts.
VI. Chemistry of Foodstuffs. By Heinr. Beckurts.
VII. Agricultural Chemistry. By A. Morgen and G. Fingerling.
VIII. Fuels and Explosives. By C. Haeussermann.
IX. Metallurgy. By Bernhard Neumann.
X. Inorganic Chemical Industries. By Gustav Keppeler.
XI. Technology of the Carbohydrates. By A. Herzfeld and Herm. Zimmermann.
XII. Fermentation Industries. By M. Delbrück and O. Mohr.
XIII. Technology of Fats and Petroleum. By J. Lewkowitsch.
XIV. Chemistry of Tar and Dyes. By P. Friedlaender.
XV. Chemical Technology of Textile Fabrics. By Edmund Knecht.
XVI. Tanning. By M. Nierenstein.

XVII. Photography. By J. M. Eder and E. Valenta.

It is interesting to note that the longest section is that relating to Organic Chemistry. This occupies 123 pages; Physical Chemistry, 72 pages; and Inorganic Chemistry, 54.

I. R.

THE PRINCIPLES OF ORGANIC CHEMISTRY. By JAMES F. NORRIS, PH.D., Professor of Chemistry in Simmons College, Boston. International Chemical Series. HENRY P TALBOT, PH D., Consulting Editor. New York and London: McGraw-Hill Book Co. 1912. Pp. v + 566. Price, $2.50.

In the preface the author states: "This book is the outcome of a number of years' experience in teaching the elements of organic chemistry to classes of beginners in the subject. In it an attempt has been made to emphasize the fundamental principles of the science and to describe in some detail the organic compounds of practical importance. The substances considered have been selected from this point of view. As a consequence, many compounds of interest to the more advanced student have been omitted; the space gained in this way has been devoted to a fuller consideration of the more important typical reactions of organic compounds and the applications of the science have been treated at greater length than is customary in elementary text-books."

The order followed in discussing the various classes of compounds differs from that usually made use of in text-books of this kind. The author refers the radicals to hydrogen as the standard, calling those more basic than hydrogen positive and those more acid negative. Alcohols consist, then, according to him, of a positive radical in combination with the hydroxyl group and acids of a negative radical with this group. This view leads the author to consider acids *immediately after the alcohols have been described*. Then he takes up ethers, anhydrides and esters, compounds which, according to him, contain, respectively, two positive radicals, two negative radicals and one positive and one negative radical linked to oxygen. The classing of these three types of compounds together makes it possible, according to the author, to bring out the relationship between the properties of compounds and the character of the radicals they contain. The consideration of alkyl and acyl halides and of amines and amides in a similar way, according to him, facilitates markedly the study of the properties of these compounds. Unfortunately the result of this is that the alkyl halides, usually considered, on account of their simplicity, immediately after the hydrocarbons, are not taken up till Chapter XII and the consideration of the amines is postponed till Chapter XI.

The carbohydrates, fats, proteins and dyestuffs are treated much more fully than is customary in elementary text-books on organic chemistry. In Chapter XVII the methods used in the identification of organic substances are described and illustrated by examples. The experience of the author has convinced him that this kind of work has great pedagogical value and can replace profitably a part of the synthetic work of the student. Problems are given at the end of most of the chapters and the author states that the solution of such problems has been found of the greatest value to the student.

The book contains some errors, which are, however, not very serious and can be easily corrected in a later edition of the book. For example, on page 27, it is stated that magnesium may be used instead of zinc in the preparation of methane from methyl iodide and then it is stated that magnesium methyl iodide with water yields methane, magnesium hydroxide and magnesium iodide, whereas the reaction of zinc methyl iodide with water is given as follows:

$$Zn\begin{matrix}CH_3\\I\end{matrix} + HOH = Zn\begin{matrix}OH\\I\end{matrix} + CH_4$$

On page 61 it is stated that isoprene is converted into India rubber when it is treated with concentrated hydrochloric acid. It is very doubtful whether India rubber can be made in this way. At any rate, Tilden, who claims to have made India rubber by this method, has never been able to repeat the experiment and no other worker in this field has ever succeeded in making India rubber in this way.

The statement on page 522 that fluorone dissolves in alkalies to form fluorescent solutions is incorrect. Fluorone is insoluble in alkalies and advantage is taken of this fact to separate it from phenolphthalein. On page 523 it is stated that *chrysolin* or *uranin* is benzylfluorescein. *Chrysolin* is *probably* the disodium salt of benzylfluorescein, while *uranin* is the disodium salt of fluorescein. Eosin, mentioned on the same page, is not tetrabromofluorescein, but the disodium salt of that compound. The formula given for guanine on page 556 is incorrect.

The book is well printed and bound and contains a large amount of information. In the opinion of the reviewer, however, it is not adapted to the use of beginners in organic chemistry.

W. R. O.

THE PREPARATION OF ORGANIC COMPOUNDS. By E. DEBARRY BARNETT, B.Sc. (LOND.), A.I.C. With 50 illustrations. Philadelphia: P. Blakiston's Son & Co. 1912. Pp. xvi + 310. Price, $2.75.

In this book "the author has aimed at giving a general out-

line of the methods actually employed in preparing organic compounds, and thus providing not only a laboratory manual, but also a book which may be used as a companion volume to the usual theoretical text-books."

In the first chapter, apparatus, methods of manipulation and reagents are considered and then follow methods for the preparation of the various hydrocarbons and their derivatives in the succeeding chapters. No attempt is made to separate the preparation of the paraffin hydrocarbons and their derivatives from those of the aromatic compounds or the preparation of the unsaturated from the saturated compounds. The first experiment given is the preparation of ethylbenzene and shortly after this comes that of menthene and dipentene. From this it will be seen that the book is not intended or at any rate is not suited to those beginning the subject of organic chemistry. The descriptions of the processes given are generally very brief and for the most part taken literally from the original articles without any change or explanations, so that unless a student has already had some experience in working in an organic chemical laboratory he would hardly be able to use this book profitably. A considerable number of the preparations have been taken from the patent literature and the author states that by this means he hopes to familiarize the academic chemist with a much neglected branch of the literature. The book seems to contain but few errors and these are of minor importance. For example, on page 39, the formulas for dipentene hydrochloride and dipentene both lack a hydrogen atom, and on page 239 it is stated that: "Some *diazo-chlorides*, however, notably those of sulphanilic and naphthionic acids, are insoluble in water and separate out." Of course, this is wrong, for neither sulphanilic acid nor naphthionic acid form diazonium chlorides when diazotized. They give inner ammonium salts, the diazonium sulphonates. The author uses diazo-salt and diazo-chloride quite frequently where it would be better to say diazonium salt. In some cases the directions are manifestly too brief. For example, in the preparation of phenolphthalein no mention is made of fluorone, nor is the student told how to remove it from the phenolphthalein which it always accompanies.

The book is well printed and bound and has a good index. In the hands of advanced students of organic chemistry it will probably be of value. W. R. O.

MODERN RESEARCH IN ORGANIC CHEMISTRY. By F. G. POPE, B.Sc. (LOND.), F.C.S. With 261 Diagrams. London: Methuen & Co., Ltd. Pp. xii + 324. Price, 7 s. 6 d.

The book is divided into nine chapters entirely independent

of each other: The Polymethylenes, 38 pages; the Terpenes and Camphors, 62 pages; the Uric Acid or Purine Group, 24 pages; the Alkaloids, 75 pages; the Relation between the Color and Constitution of Chemical Compounds, 22 pages; Salt Formation, Pseudo Acids and Bases, 23 pages; the Pyrones, 30 pages; Ketenes, Ozonides, Triphenylmethyl, 22 pages; the Grignard Reaction, 20 pages.

In the first four chapters and in that on the pyrones, a large number of representatives of the groups of compounds under discussion are taken up and the reactions, synthetical and analytical, by which their constitutions have been determined, are given. Structural formulas are used lavishly. To the reviewer, it seems that if fewer compounds had been discussed and the relationship of one to the other brought out more clearly, the result would have been a more interesting book. As it now stands, the reader soon wearies of the multitude of equations and formulas given; it is not a book which can be read for the pleasure of it, and its chief use will probably be found in that it gives briefly and diagramatically the series of reactions by which the constitutions of the compounds discussed have been worked out. The chapter on the Grignard reaction suffers from the same disadvantage.

The other chapters are more interesting. That on the relation between color and constitution takes up briefly the chromophore and auxochrome theories, the quinonoid theory, Baeyer's "carbonium valency," and Baly's "isorropesis" theory. In the chapter on salt formation are discussed, all too briefly, oxonium and carbonium salts. Hantzsch's views on pseudo acids and bases receive somewhat more extended and adequate treatment. The few pages devoted to ketenes, ozonides and triphenylmethyl will be read with interest. These chapters could have been made longer at the expense of the others without detracting from the value of the book.

References to the more inportant articles bearing on the subject are appended to each chapter. Although published in 1912, the book seems to have been written almost entirely about 1909, as very few pieces of work done since then are given mention.

In the first edition of a book involving so many equations, typographical errors are bound to occur, but the number of such errors found in the present volume is inexcusably large.

C. A. R.

THE INTERPRETATION OF RADIUM, being the Substance of Six Free Popular Experimental Lectures delivered at the University of Glasgow. By FREDERICK SODDY, M.A., F.R.S., Independent Lecturer in Physical Chemistry and Radioactivity in the University of Glasgow. With Illustrations. Third Edition, Revised and Enlarged. New York: G. P. Putnam Sons. 1912. Pp. xvi + 284. Price, $2.00.

This interesting book is a statement in popular and somewhat flowery language of the well-known facts in connection with radioactivity. There are some defects to which the reviewer must call attention. On page 18 we read, "The juxtaposition of radioactivity and transmutation is not a fanciful one, because it will appear, as we proceed, that the two processes are most intimately connected." The spontaneous production of helium from the radium emanation bears no relation to transmutation of the elements, as I have repeatedly pointed out. The spontaneous production of one substance from another, at a rate which can not even be varied, by any means known to man, is one thing; and the production of one element from another by artificial means, which is what the alchemists meant by 'transmution,' is obviously an entirely different matter. The latter problem is apparently as far from being solved as it was in the days of the alchemists.

One other point in reference to the book as a whole. The facts of radioactivity would to-day be just so many empirically established facts, without any possibility of explanation, were it not for the work of Sir J. J. Thomson on the electron, which preceded the discovery of radioactive phenomena. If Thomson had not shown that the simplest chemical atom is tremendously complex; if he had not overthrown the older chemical conception of the atom that it was a simple ultimate unit of matter, we could never have had the present theory of radioactivity.

Thomson not only showed that the atom is complex, but in what its complexity consisted, in rapidly moving electrons. This made possible the theory of the *unstable atom*, which underlies the explanation of all radioactivity. There is not enough stress laid upon this fact, and not enough credit given Thomson by the author of this book. With this exception the defects in the work are of minor consequence. H. C. J.

EXPERIMENTAL RESEARCHES ON THE SPECIFIC GRAVITY AND THE DISPLACEMENT OF SOME SALINE SOLUTIONS. By J. Y. BUCHANAN, M.A., F.R.S., Chemist and Physicist of the Challenger Expedition. Reprinted from the Transactions of the Royal Society of Edinburgh, Vol. XLIX, Part 1. Edinburgh: Neill & Co., Limited. 1912. Pp. 227. Price, 7 s. 6 d.

In this monograph the author gives a detailed account of his important investigations on the determination of the specific

gravity of salt solutions. Since the year 1871, when he was appointed chemist and physicist to the "Challenger" expeditions, he has been more or less continuously engaged in studying precise methods for the determination of specific gravity. After considering the relative merits and defects of all of the well-known methods for the determination of density he chose the hydrometric method since, to quote his own words, "the hydrometer appeared to be the only type of instrument which furnished *directly* the information demanded, namely, the specific gravity of the water, and that with the exactness required when the variations of specific gravity are so small."

It is a matter of no little surprise to learn that this experimenter has brought the hydrometric methods to such a high state of perfection that it is possible to determine specific gravities to six places of decimals, with a probable error of less than three units in the sixth place. Tables are given of the specific gravities of solutions of the chlorides, bromides, iodides, chlorates, bromates, iodates, and nitrates of the alkali metals, together with similar data for some salts of the metals of the alkaline earths.

In one of the last sections of the work the author calls attention to a remarkable state of unrest observed in supersaturated solutions of calcium chloride before crystallization. This is one of the most interesting chapters of the monograph and has an important bearing upon the mechanism of crystal formation.

Chemists and physicists owe Mr. Buchanan a debt of gratitude for his work in refining the hydrometric method for the determination of specific gravity and also for the very valuable tables he has compiled. This monograph should be in the possession of every one who has occasion to make precise determinations of specific gravity.

FREDERICK H. GETMAN

WATER, ITS PURIFICATION AND USE IN THE INDUSTRIES. By WILLIAM WALLACE CHRISTIE, Consulting Engineer. New York: D. Van Nostrand Company. 1912. Pp. xi + 219. Price, $2.00.

This book, intended primarily for engineers, contains descriptions of processes and apparatus for the softening, purifying, removing of oil and measuring of water. Great pains has apparently been taken by the author to make these descriptions not only accurate but readily understood, and in most instances he has admirably succeeded. He is not so fortunate in his treatment of so-called "Impurities of Water," which discusses the mineral constituents. For example, the impression is given that calcium and magnesium occur in water as the normal carbonates. The chapter on "Drinking Water" might be improved by rearranging and sorting the data; and

the statement on page 2 that "Albuminoids and free ammonia get into water supplies through the run-off water and give rise to many epidemics" is somewhat surprising.

A chapter containing information which might be useful to the engineer dealing with water supplies and water works is well put together. The text is amply illustrated with excellent cuts. As a whole, the book should be of considerable value to engineers.

G. F. NORTON

DAS ERDÖL, SEINE PHYSIK, CHEMIE, GEOLOGIE, TECHNOLOGIE AND SEIN WIRTSCHAFTSBETRIEB. In fünf Bänden. Herausgegeben von C. ENGLER, o. ö. Professor an der Techn. Hochschule zu Karlsruhe, und H. v. HÖFER, o. ö. Professor an der Montanistischen Hochschule zu Leoben, unter Mitwirkung von verschiedenen Gelehrten. I. Band, zweite Abteilung mit Tabellen-Beilage. Leipzig: Verlag von S. Hirzel. Pp. xvii + 262. Price, M. 22.00.

This deals first with a brief description of the properties and physical characters of all the known crude petroleums, arranged by countries, completing Part III. Part IV considers the congeners of petroleums, ozokerite, asphalt and natural gas. Part V treats of the physiological action of petroleum and its products.

The tables give analyses of typical oils from all the various countries.

The first volume has already beeen reviewed.[1]

A. H. GILL

FATTY FOODS: Their Practical Examination. A Handbook for the Use of Analytical and Technical Chemists. By E. RICHARDS BOLTON, F.C.S., Consulting Analyst and Technical Chemist, and CECIL REVIS, Chief Chemist, Messrs. Welford & Sons, Ltd. Philadelphia: P. Blakiston's Son & Co. 1913. Pp. x + 371. Price, $3.50.

In this volume the examination of fatty foods is regarded entirely from the edible standpoint. The authors presuppose a general knowledge of the chemistry of fats and oils and then give methods for the analysis of a large number of these compounds, from both animal and vegetable sources, together with the results which they have obtained by the outlined method.

F. P. UNDERHILL

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The Index to Volume XLIX of THIS JOURNAL will appear in the July number.

[1] THIS JOURNAL, 48, 472.